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A REVIEW OF AIR POLLUTANT DAMAGE TO MATERIALS

Prepared by:

John E. Yocom, P.E.
and
Alexander R. Stankunas, Ph.D.
TRC Environmental Consultants, Inc.
Wethersfield, CT

and

F. Vandiver P. Bradow
Environmental Criteria and Assessment Office
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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Report prepared as U.S. contribution to Panel 3 of NATO Committee on Challenges of Modern Society Pilot Study on Air Pollution Control Strategies and Impact Modeling. Panel 3 focuses on air pollutant impact and will publish 4 reports on air pollutants effects; this is the first in the series and covers effects on materials. Reviewed here are physical and economic effects of sulfur oxides, particulate matter, nitrogen oxide, ozone, hydrogen sulfides, fluoride, and ammonia on metals, textiles, paint, building materials, leathers, paper and elastomers. Report is summary of pertinent information in EPA's air quality criteria and EPA-Funded NAS review documents.

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1. PHYSICAL DAMAGE

1.1 INTRODUCTION

There is no question that the presence of air pollutants, notably sulfur oxides, particulate matter, nitrogen oxides, and ozone under the proper circumstances can exacerbate damage to non-living materials thereby producing costs to society. Material damage related to air pollution has been recognized for well over 300 years. In 1661 John Evelyn, a public spirited citizen of London, described the air pollution situation in London as follows (Evelyn, 1933)[*]:

> "This is the pernicious Smoake which sullyes all her Glory, superinducing a sooty Crust or Fur upon all that it lights, spoyling the moveables, tarnishing the Plate, Gildings and Furniture, and corroding the very Iron-bars and hardest Stones with these piercing and acrimonious Spirits which accompanying its Sulphure; and executing more in one year, than exposed to the pure Aer of the Country it could effect in some hundreds.
>
> It is this horrid Smoake which obscures our Churches, and makes our Palaces look old, which fouls our Clothes, and corrupts the Waters, so as the very Rain, and refreshing Dews which fall in the several Seasons, precipitate this impure vapour, which, with its black and tenacious quality, spots and contaminates whatever is exposed to it."

His pointing out of sulfur and acid rain as causative agents appears prophetic, but "sulphure" as used in his pamphlet undoubtedly had more to do with emanations from the nether regions than any special knowledge of sulfur chemistry as related to air pollution effects.

The term "Acid Rain" refers to poorly understood phenomenon which has only recently drawn the attention of the scientific community in the U.S. The term has been widely and indiscriminately used to describe a syndrome in which gases are not acrdic when emitted, and only become acidic after conversion. Gases such as sulfur and nitrogen oxides are emitted from combustion sources, may be transported many miles, converted to sulfates and nitrates, and deposited in or along with rain on sensitive ecosystems. The impact of "acid rain" on non-living materials, buildings and monuments is frequently cited as one of the serious consequences of this scenario. This assertion is made even though the greatest number of exposed materials are located near the sources and not in the sylvan or rural settings usually associated with "acid rain" effects.

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[*] References appear at the end of this chapter.

In an attempt to broaden the understanding of what "acid rain" really is and to help explain the fact that there is uncertainty in determining cause and effect, the term "acidic deposition" is now wider used to describe this syndrome. This broader term permits the inclusion of effects on materials such as metal corrosion or stone damage that appear to be related more to reactions between gaseous pollutants such as SO_2 and moist surfaces than damage from pre-acidified rain water.

Table 1-1, based on a review by Yocom and Upham, summarizes the types of damage that can be caused by air pollution (Yocom and Upham, 1977). The important points to be brought out from Table 1-1 are:

- A variety of materials are damaged by common air pollutants.
- Sulfur oxides figure prominently as a pollutant type which can cause damage to many materials.
- Air pollution is only one of the environmental factors that can cause damage to materials exposed to outdoor atmospheres.

There are several fundamental problems in quantifying the extent of damage to materials from specific pollutants:

- The types of damage associated with air pollutants tend to occur in unpolluted atmospheres and cannot be distinguished from those caused or enhanced by the presence of air pollutants. Damage can be produced by moisture, SO_2,

TABLE 1-1. AIR POLLUTION DAMAGE TO MATERIALS

Materials	Type of damage	Principal air pollutants	Other environmental factors
Metals	Corrosion, tarnishing	Sulfur oxides and other acid gases	Moisture, air, salt, microorganisms
Building stone	Surface erosion and discoloration	Sulfur oxides and other acid gases, particulate matter	Moisture, temperature fluctuations, salt, vibration, microorganisms, CO_2
Paint	Surface erosion, discoloration	Sulfur oxides, hydrogen sulfide, ozone, particulate matter	Moisture, sunlight, microorganisms
Textiles	Reduced tensile strength, soiling	Sulfur oxides, nitrogen oxides, particulate matter	Moisture, sunlight, physical wear
Textile dyes	Fading, color change	Nitrogen oxides, ozone	Sunlight
Paper	Embrittlement	Sulfur oxides	Moisture, physical wear
Rubber	Cracking	Ozone	Sunlight, physical wear
Leather	Weakening, powdered surface	Sulfur oxides	Physical wear
Ceramics	Changed surface appearance	Acid gases, HF	Moisture, microorganisms

Source: Adapted from Yocom and Upham, 1977.

natural particulate matter, sunlight and other features of the natural environment. Thus, determining the isolated influence of a given pollutant in an ambient exposure situation is not a straightforward process.

- Laboratory studies where individual pollutants are introduced to sensitive materials in known exposures independent of other influences tend to be operated at unrealistically high concentrations and otherwise are not representative of real life exposure situations.
- Reduction in ambient levels of pollutants such as SO_2 as the result of air pollution control efforts has significantly reduced the exposure and degree of possible damage to exposed materials. Damage identified and measured today may have been the result of much earlier exposure when concentrations were much higher.
- Changes over recent years in the types of materials and protective coatings exposed to the atmosphere as a result of technological improvements in materials is having a fundamental effect upon the nature and extent of air pollution-induced damage to materials and associated damage costs.
- Determination of the quantities of materials in place in relation to air pollutant exposures is a difficult task, especially when significant amounts of certain materials (e.g., fabrics, paints and paper) may be exposed to indoor environments or other locations not represented by typical ambient monitors.

The Air Quality Criteria Documents for particulate matter, sulfur oxides, nitrogen oxides and ozone contain thorough reviews of the literature on material effects related to each of the pollutant classes (Bradow, 1981; U.S. Environmental Protection Agency, 1979; 1978). This chapter will rely heavily upon the parts of those documents dealing with material effects, but will not attempt to comment on all of the primary documents referred to. Rather, those pieces of original work or reviews believed by the author to be most significant will be referred to, plus any other significant published work reported since the dates of the criteria documents.

1.2 SULFUR OXIDES

From Table 1-1 it is apparent that sulfur oxides figure prominently in many types of air pollution-induced damage to materials. Sulfur dioxide (SO_2), the principal sulfur oxide emitted to the air, originates primarily from the burning of sulfur-containing fuels and from the roasting of sulfide ores in the winning of certain non-ferrous metals. The exact mechanism by which SO_2 and other sulfur oxides damage materials are not known, but invariably moisture and oxidation to sulfates are required. There are many possible scenarios for the damage to materials by sulfur oxides, three of which are described as follows:

1. SO_2 is absorbed in moisture (condensed or from precipitation) on surfaces and is oxidized to sulfates.
2. SO_2 is oxidized to sulfates in the atmosphere and deposited on surfaces which are already wet through condensation or precipitation.
3. Rain water containing sulfates and dissolved SO_2 from the upper air or scavenged from the air falls on sensitive surfaces.

The last mentioned of these might be considered as a description of the "acid rain" syndrome alluded to earlier. The surfaces of material susceptible to air pollution damage exist in greatest abundance in urban and industrial areas close to sources of primary pollutants and not in those remote areas where "acid rain" is believed to be a problem. Furthermore, it is likely that more material damage occurs from direct contact of SO_2 and sulfates on moist surfaces than from acidic rain falling on the surfaces. As pointed out in the Introduction, the term "acidic deposition" which is supplanting the term "acid rain" would include all of the anticipated mechanisms by which sulfur oxides contact and affect materials.

Judeikis and Stewart (1976) have shown that SO_2 deposition velocities for a variety of materials vary widely. Of these materials tested in a flow reactor, a cured cement had the highest value, 2.5 cm/sec, with asphalt exhibiting the lowest value, 0.04 cm/sec. No metals were tested in this experiment. Deposition velocities decreased as the surface became saturated with SO_2. Humidity increased the capacity of the surface to absorb or adsorb SO_2. The reactivity of the surface could be restored by washing or exposing the spent surface to ammonia.

1.2.1 Ferrous Metals

Corrosion of iron and steel in polluted atmospheres has received a great deal of attention over the years. The draft criteria document prepared by the Environmental Protection Agency (Bradow, 1981) to support air quality standards for particulate matter and sulfur oxides (PM/SO_x) contains an extensive review of the possible mechanisms for metal corrosion in the presence of sulfur oxides.

Some of the earliest work on the nature of iron corrosion in atmospheres containing sulfur oxides was that of Vernon (1935). He showed the relative roles of SO_2 and humidity and proposed that there are critical humidities for the corrosion of metals above which SO_2 induced corrosion proceeds rapidly. He also showed that corrosion of iron proceeds from randomly distributed centers which he associated with the deposition of particulate matter. However, it may also be likely that these "centers" represent differences in the grain structure of the sample. These differences produce electrochemical cells which with a moist, conducting surface, allow current to flow and corrosion to proceed.

Many workers have advanced theories explaining the principal chemical reactions that describe iron and steel corrosion in the presence of SO_2. A variety of chemical routes are possible and it is likely that several of them operate in real life atmospheric exposures. Those interested in the research on which these theories are based are directed to the references listed in the chapter on materials in the PM/SO_x criteria document (Bradow, 1981). This report will not attempt to cover such background material.

According to Barton (1976), once corrosion has been initiated, the progress of the reaction is controlled largely by sulfate ions produced from the oxidation of absorbed or adsorbed SO_2. However, the actual mechanism of SO_2 oxidation on the surface is poorly understood. The work of Johnson et al. (1977) in England appears to show that sulfur or sulfates are only a minor constitutent of the corrosion products of steel. Mild steel samples were exposed to two urban areas near Manchester. One area was heavily polluted, and the other was lightly polluted. Scanning electron microscopy energy dispersive x-ray analysis and x-ray diffraction analysis of corrosion products showed them to be predominantly $\gamma\cdot Fe_2O_3\cdot H_2O$, $\alpha\text{-}Fe_2O_3\cdot H_2O$ and $\alpha\cdot FeOOH$. Some minor amounts of sulfur were found in a few of the samples. The relative amount of corrosion produced was strongly dependent on whether or not the sample was initially wet at the beginning of the exposure.

Rust tends to protect iron and steel from further corrosion. Nriagu (1978) and Sydberger (1978) reported that steel samples exposed initially to low concentrations of sulfur oxides were more resistant to further corrosive attack than samples exposed continuously to high concentrations.

The long-term corrosion rate of steel appears to depend on changes in the composition and structure of the rust layer. During the initiation period, which varies with the SO_2 concentration and other accelerating factors, the rate of corrosion increases with time (Barton, 1976). Because it is porous and nonadherent, the rust initially formed offers no protection; in fact, it may accelerate corrosion by retaining hygroscopic sulfates and chlorides, thus producing a microenvironment with a high moisture content. After the initiation stage, the corrosion rate decreases as the protective properties of the rust layer improve. Satake and Moroishi (1974) relate this slowing down to a decrease in the porosity of the rust layer. During a third and final stage, corrosion attains a constant rate and the amount of SO_4^{2-} in rust is proportional to atmospheric SO_x concentrations.

1.2.1.1 Laboratory Studies--Exposing iron and steel samples to SO_2 and humidity under controlled laboratory conditions has two principal advantages:

1. The pollutant concentrations and other influencing factors can be independently controlled in a factorial experiment and permit the quantification of each factor's impact.
2. Exposure conditions can be made more severe than in nature to accelerate the corrosion effect, thereby reducing the duration of the experiment.

While many of the early experiments showed clearly that corrosion rates correlate with both SO_2 and humidity, exposure consisted of SO_2 concentrations many times higher than those found in the ambient atmosphere or what are referred to as "reflux" conditions, where water and excess SO_2 were continually flushing the surface of the samples.

The most realistic set of laboratory experiments was conducted by Haynie et al. (1976). The primary advantages of this study over previous laboratory studies include the following:

- Pollutant concentrations (SO_2, NO_2 and O_3) were controlled at levels that encompass those found in ambient urban atmospheres.
- Experiments were statistically designed for analysis of variance and the degree of interaction between pollutants and other environmental stresses.

- Sunlight was simulated by a xenon arc light which approximates the spectrum of sunlight.
- "Weathering steel", material used unprotected in the ambient atmosphere, was used for the steel sample. Many of the previous studies used mild steel or enameling steel which would not normally be used unprotected.

Steel corrosion was determined in terms of weight loss of the steel panels. As might be expected, the results showed that there was a strong, statistically significant relationship between steel corrosion and SO_2 concentration, together with high humidity.

1.2.1.2 Field Studies--A problem inherent with field studies is that iron and steel corrosion occurs even in unpolluted atmospheres, and the specific impact of SO_2 is difficult, if not impossible, to isolate completely. Therefore, the effects of SO_2, along with moisture, can only be inferred by statistical treatment of the data.

Upham (1967) exposed mild (low-carbon structural) steel samples in a number of sites in and around St. Louis and Chicago. He showed that corrosion correlated well with sulfur oxide levels and increased with length of exposure. Haynie and Upham (1971) continuously monitored urban pollutants including SO_2, NO_2, and O_3 (oxidants) to determine whether previously unconsidered variables might affect steel corrosion. They also considered temperature RH, and TSP. Their 5-year program, begun in 1963, involved sites in Chicago, Cincinnati, New Orleans, Philadelphia, San Francisco, Washington, Detroit, and Los Angeles. They studied three types of steel expected to show different levels of resistance to atmospheric corrosion: (1) a plain carbon steel containing some copper (0.1 percent copper); (2) a copper-bearing steel (0.22 percent copper); and (3) a low-alloy weathering steel (0.4 percent copper with 0.058-percent phosphorus). The exposure periods were 4, 8, 16, and 32 months. The same steels were exposed at rural sites as a control. The rural sites proved to have higher than expected corrosion rates; however, SO_2 concentrations were not measured at these sites. Multiple regression analysis established significant correlations between average SO_2 concentrations and corrosion of all three steels at the urban sites. Temperature was a statistically insignificant variable. Average RH was insignificant because the range was only between 62 and 77 percent.

In another study Haynie and Upham (1974) exposed enameling steel containing 0.019-percent carbon and 0.028-percent copper at 57 sites in NASN. They measured corrosion by weight loss and quantitatively determined other pollutants, including gaseous SO_2, TSP, and the amount of SO_4^{2-} and NO_3^- in the particles. Sulfur dioxide levels ranged from 9 to 374 μg/m^3, TSP from 11 to 182 μg/m^3, and RH from 29 to 76 percent. The average temperature remained within a fairly narrow range and was considered constant. The temperature, the quantity of total particles, and the presence of NO_3^- in the particles did not significantly affect the corrosion rate of steel. The concentration of SO_2 was significant only when SO_4^{2-} was not included in the regression analysis. At each site, SO_4 content of the particles and SO_2 concentration were closely related. On the basis of this study, Haynie and Upham derived the following empirical expression to obtain the best relationship between corrosion of enameling steel and atmospheric SO_2 content:

$$\text{Corrosion} = 325t^{\frac{1}{2}}e^{(0.00275\ SO_2\ -\ 163.2/RH)}$$

where: corrosion is expressed as μm

SO_2 is expressed as μg/m^3

RH = relative humidity (percent)

t = time

Average RH is a substitute variable for the fraction of time the steel is wet.

Figures 1-1 and 1-2 show plots of pseudo corrosion rate ($cor/\sqrt{t}$) versus relative humidity and SO_2 concentrations, respectively. Comparison of these two graphs shows that the sensitivity of corrosion to humidity is far greater than that for SO_2, especially at levels of SO_2 normally experienced in urban areas.

For example, referring to Figure 1-1, if one were comparing relative corrosion at 55 percent relative humidity in two areas with average levels of 80 and 160 $\mu g/m^3$, a very significant difference in relative air pollutant levels, the difference in relative corrosion would be only 3 percent. On the other hand, from Figure 1-2, if one were comparing relative corrosion at a constant SO_2 level of 100 $\mu g/m^3$ between two areas with a moderate difference in average relative humidity (55 and 65 percent), the difference in relative corrosion rate would be 14 percent.

Other damage functions relating steel corrosion to SO_2 and humidity (or time of wetness) have been developed by Chandler and Kilcullen, (1968) and Guttman and Sereda (1968).

A more recent study of material damage in the St. Louis area in 1974-75 by Mansfeld (1980) included the use of special atmospheric corrosion monitors

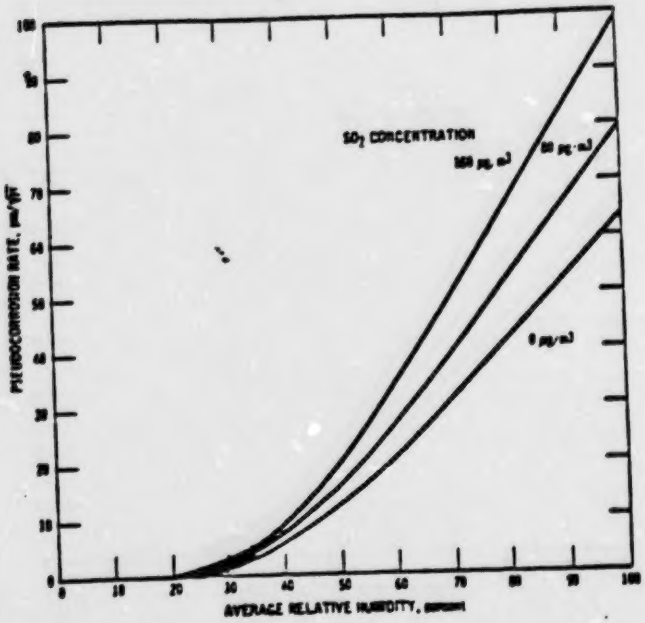


FIGURE 1-1. Steel corrosion behavior as a function of average relative humidity at three average concentration levels of sulfur dioxide. (Haynie and Upham, 1974).

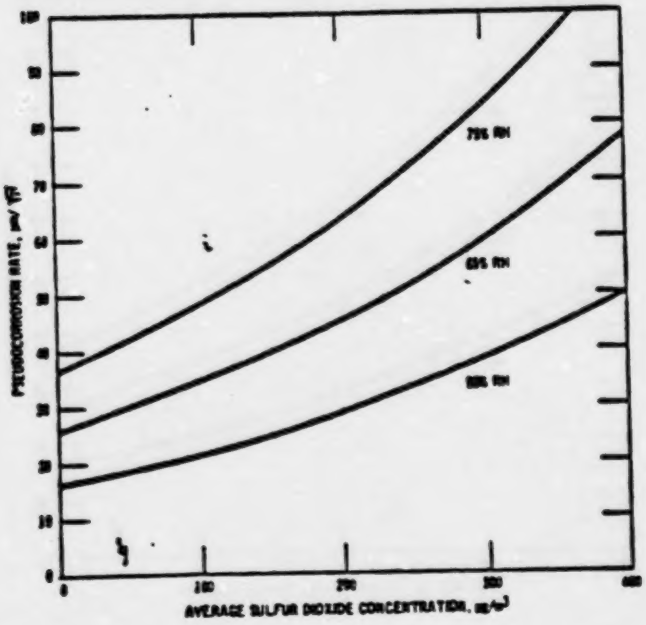


FIGURE 1-2. Steel corrosion behavior as a function of average sulfur dioxide concentration and average relative humidity. (Haynie and Upham, 1974).

which measure the length of time that a corrosion panel is wet enough for electrochemical corrosion to take place. His sample exposure array included weathering steel, galvanized steel, house paint and marble. Concentrations of SO_2 measured in this study were an order of magnitude lower than those measured by Upham's 1957 study (Upham, 1967). The low concentrations of SO_2 may be one of the reasons Mansfeld was not able to show any significant correlation between corrosivity and pollutant levels. More likely, however, is that difficulties with the time of wetness proxy data (relative humidity, RH) precluded inclusion of RH in the data analysis.

1.2.1.3 Areas of Needed Research--While much effort has been expended in defining the mechanisms of attack of SO_2 and moisture on iron and steel, one cannot help but wonder how important this problem is in view of the following factors:

- Except for weathering steel, there is a question of how much unprotected steel is actually in service.
- Levels of SO_2 in the United States and other parts of the world have been reduced significantly through control efforts, and may exert only an insignificant effect on iron and steel corrosion.

Before more research is carried out on the mechanisms of damage, studies directed at the above two questions should be initiated.

Gerhard and Haynie (1974) have given some limited consideration to a possible role of air pollutants (notably SO_2) in catastrophic failure of metals -- largely in relation to stress corrosion. This is an extremely complex area and one susceptible to misinterpretation because of the potential for significant accidents which endanger human lives. An independent assessment should be made of this entire area coupled with laboratory research to assess its importance, especially in an era of decreasing (or stabilizing) air pollutant levels.

1.2.2 Nonferrous Metals

The corrosion rates of commercially important nonferrous metals in polluted atmospheres, although generally less than those for steel, cover a wide range. The relative corrodibility of some of these nonferrous metals can be compared in Table 1-2. This summary of 20 years of investigation by the ASTM Committee on Atmospheric Corrosion compares corrosion rates for different metal formulations and under different exposure conditions (Copson, 1955).

Assuming that Altoona, PA and New York, NY represented locations with high SO_2 and particulate matter concentrations in the period 1930-54, it is clear that nickel and zinc are the most susceptible of the six metals studied. Of these two, zinc is by far the more important because of its extensive use in galvanizing to protect steel in the ambient atmosphere.

Figure 1-3 from the work of Sydberger and Vannerberg (1972) shows adsorption of SO_2 with time at 90 percent relative humidity for iron and three nonferrous metals. The characteristics of these curves appear to correlate with the relative susceptibility of the metals to SO_2 attack.

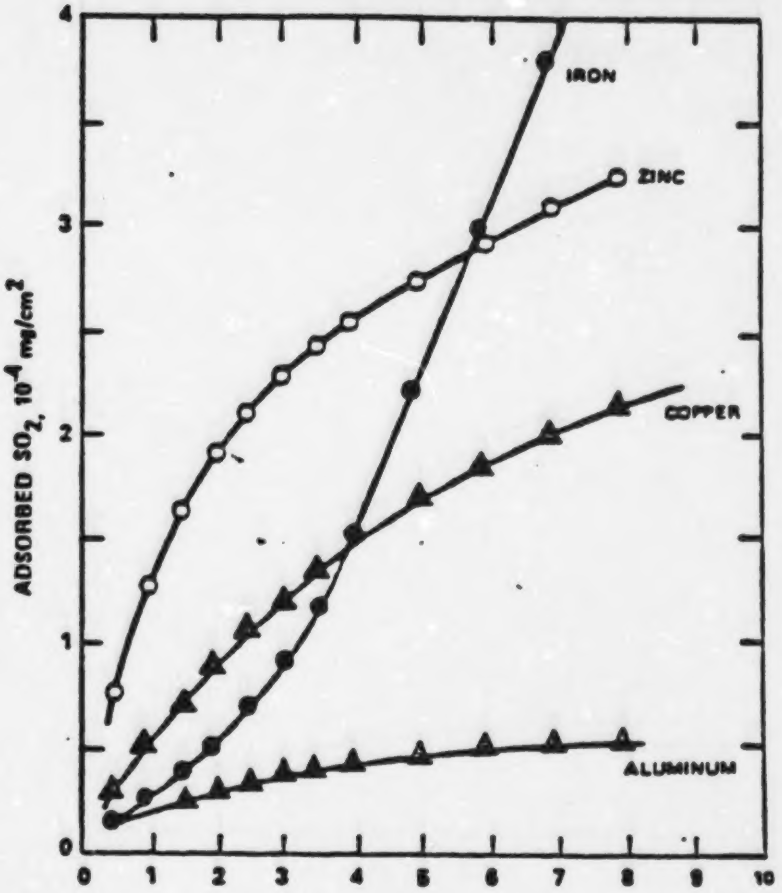
1.2.2.1 Aluminum--Aluminum is considered to be quite resistant to SO_2-induced corrosion because of the highly inert oxide layer formed on the surface. However, the presence of high concentrations of particulate matter can produce a mottled or pitted surface in the presence of SO_2. Fink et al. (1971) summarized measured corrosion rates and depth of pitting of aluminum surfaces in rural, mild industrial (30 $\mu g/m^3$ or 0.01 ppm SO_2), normal industrial (370 $\mu g/m^3$ or 0.14 ppm SO_2 and 80-percent RH), and severe industrial areas. Their overall conclusion was that, although some loss of thickness occurred in the first 2 years, structures composed of aluminum and its alloys are resistant to air pollutants. In view of efforts to control emissions of SO_2 and particulate matter in the United States--especially larger particles or agglomerates that

TABLE 1-2. WEIGHT LOSS OF METAL PANELS[a] AFTER 20 YEARS EXPOSURE IN VARIOUS ATMOSPHERES (ABOUT 1930 - 1954)

City	Exposure classification	Average loss in weight, %					
		Commercial copper (99.9% + Cu)	Commercial aluminum (99% + Al)	Brass (85% Cu, 15% Zn)	Nickel (99% + Ni)	Commercial lead (99.92% Pb, 0.06% Cu)	Commercial zinc (99% Zn, 0.85% Pb)
Altoona, Pennsylvania	Industrial	6.1	---	8.5	25.2	1.8	30.7
New York, New York	Industrial	6.4	3.4	8.7	16.6	---	25.1
La Jolla, California	Seacoast	5.4	2.6	1.3	0.6	2.1	6.9
Key West, Florida	Seacoast	2.4	---	2.5	0.5	---	2.9
State College, Pennsylvania	Rural	1.9	0.4	2.0	1.0	1.4	5.0
Phoenix, Arizona	Rural	0.6	0.3	0.5	0.2	0.4	0.8

[a] Panels - 9 x 12 x 0.035 in (22.86 x 30.48 x 0.089 cm).

Source: Copson, 1955.



EXPOSURE TIME, hr

FIGURE 1-3. Adsorption of sulfur dioxide on polished metal surfaces is shown at 90 percent relative humidity.

Source: Adapted from Sydberger and Vannerberg (1972).

could act as centers for corrosion initiation, SO_2-induced surface corrosion of aluminum does not appear to be a significant problem.

Possible stress corrosion of aluminum in the presence of SO_2 is potentially a more serious problem than surface corrosion. Haynie et al. (1976) found, as part of their extensive chamber studies, that stressed aluminum samples exposed to 79 and 1310 $\mu g/m^3$ of SO_2 lost approximately 8.6 and 27.6 percent of their bending strength, respectively.

1.2.2.2 Copper--Copper and copper alloys in most atmospheres develop thin, stable surface films, which inhibit further corrosion. Initial atmospheric corrosion is a brown tarnish of mostly copper oxides and sulfides which can thicken to a black film. Then in a few years, the familiar green patina forms. Analysis of this film indicates it to be either basic copper sulfate or, in marine atmospheres, basic copper chloride, both of which are extremely resistant to further atmospheric attack. According to Simpson and Horrobin (1970), the formation of these basic copper salts can take as long as 5 or more years and will vary with the concentration of SO_4^{2-} or chloride particles, the humidity, and the temperature. They reported the corrosion rate of copper to by 0.9 to 2.2 μm/year in industrial atmospheres, compared with 0.1 to 0.6 μm/year in rural areas.

1.2.2.3 Zinc--The primary use of zinc other than as an alloying metal with copper to produce brass, is in galvanizing steel to make it resistant to corrosion in the atmosphere. Zinc is anodic with respect to steel such that when zinc and steel are in contact with an electrolyte, the current flow protects the steel from corrosion at the expense of some oxidation of zinc.

Because of its economic importance, the behavior of zinc in polluted atmospheres has been studied intensively by a number of workers. Guttman (1968) carried long-term measurements of atmospheric corrosion of zinc in the

Birchbank area, near Trail, B.C., in Canada, starting in 1958. He developed an empirical damage function for zinc corrosion in relation to SO_2 concentrations and "time-of-wetness". Time of wetness was measured by means of a dew detector. SO_2 was measured by lead peroxide sulfation candles and conductiometric SO_2 measurements. His empirical damage function is:

$$y = 0.005461(A)^{0.8152} \times (B + 0.02889)$$

where

y = corrosion loss, mg for a 3 x 5 in. panel

A = time of wetness, hr

B = atmospheric SO_2 content during the periods the panels were wet.

Haynie and Upham (1970) carried out an extensive zinc corrosion study in eight cities where zinc panels were exposed while concurrently collecting data on SO_2, temperature and himidity. They developed the following empirical damage function relating zinc corrosion to SO_2 levels and relative humidity.

$$y = 0.001028\ (RH - 48.8)\ SO_2$$

where

y = corrosion rate, μm/yr

RH = average annual relative humidity

SO_2 = average SO_2 concentration, μg/m^3

The damage coefficients for these two functions plus functions developed from four other studies were compiled by EPA (Bradow, 1981). These coefficients are compared in Table 1-3. Note that the SO_2 coefficients vary over a factor of over four and that the chamber study (Haynie et al., 1976) has by far the lowest SO_2 coefficient. The chamber study isolated the specific influence of SO_2 and the studies carried out in the ambient atmosphere include the joint effect of SO_2 and particulate matter containing sulfates, chlorides, nitrates and other anions; thus the difference in SO_2 coefficient (and its

TABLE 1-3. EXPERIMENTAL REGRESSION COEFFICIENTS WITH ESTIMATED STANDARD DEVIATIONS FOR SMALL ZINC AND GALVANIZED STEEL SPECIMENS OBTAINED FROM SIX EXPOSURE SITES

Study	Time-of-wetness coefficient, μm/yr	SO_2 coefficient, (μm/yr)/(μg/m^3)	Number of data sets
CAMP (Haynie and Upham, 1970)	1.15 ± 0.60	0.081 ± 0.005	37
ISP (Cavender et al., 1971)	1.05 ± 0.96	0.073 ± 0.007	173
Guttman, 1968	1.79	0.024	>400
Guttman and Sereda, 1968	2.47 ± 0.86	0.027 ± 0.008	136
Chamber study (Haynie et al., 1976)	1.53 ± 0.39	0.018 ± 0.002	96
St. Louis (Mansfeld, 1980)	2.36 ± 0.13	0.022 ± 0.004	153

Source: Bradow, 1981.

direction) between the chamber study and those for outdoor exposures appears reasonable. If the two studies using lead peroxide candles (Guttman and Sereda, 1968 and Guttman, 1968) are not considered, one could infer that earlier atmospheric exposures (Haynie and Upham, 1970; Cavendar et al. 1971) represent a situation where the SO_2 coefficient greatly overpredicts the effect because of high concentrations of particulate matter and a variety of anions that also affect zinc corrosion. The recent study by Mansfeld (1980) was carried out in St. Louis after pollutant levels were greatly reduced from those found during the exposure of the 1960's, and may represent a situation more closely simulating that of the chamber studies which were carried out in the absence of particulate matter.

1.2.2.4 Areas of Needed Research--As noted above, a considerable amount of research has already been carried out on the atmospheric corrosion of zinc. Other nonferrous metals are not as important as zinc because of lesser amounts being exposed to the outdoor atmosphere, their greater resistance to SO_2 and declining SO_2 concentrations in most urban areas in the United States. However, three areas where further work is needed are:

1. Substantiation of the SO_2 damage coefficient based on present day levels of SO_2 and particulate matter in a number of cities. Development of damage coefficients for particulate matter.
2. Further study of stress corrosion of aluminum and aluminum alloys in relation to ambient SO_2 exposures.
3. Studies to evaluate the role of microorganisms in metal corrosion.

1.2.3 Paint

Paint consists of pigment and vehicle. Pigments, such as titanium dioxide and zinc oxide, provide color, hiding power, and durability. The vehicle provides the film-forming properties of the paint and contains resin binders, solvents and additives. Together the pigment and vehicle protect the underlying surface and enhance the attractiveness or neatness of the exposed surface. Air pollution may limit both of these functions by damaging the protective coating and exposing the underlying surface to attack. The most important potential effects of SO_2 on paints are interference with the drying process and acceleration of the normal erosion process.

Holbrow (1962) has reported a number of experiments to determine effects of sulfur dioxide on newly applied paints. Drying time for various oil-base paints exposed to 2620 to 5240 $\mu g/m^3$ (1-2 ppm) of sulfur dioxide was increased 50-100 percent. Films thus dried had either softer finish or, in some cases, a more brittle finish, and as a result of either change the paints were likely to provide less than optimum durability. Discoloration of Brunswick green paints were noted if the fresh paints were exposed to sulfur dioxide, warmth, and moisture. Under these conditions, the lead chromate in the pigment was bleached and became blue. It should be pointed out, however, that these experiments were carried out at SO_2 concentrations an order of magnitude or more above those usually experienced in urban atmospheres. Thus far no experiments have been carried out on the effect of SO_2 on drying time of water-based latex paints.

Campbell et al. (1974) carried out an extensive study of paint erosion for a variety of paint types and exposure conditions (including SO_2 ad O_3). Both chamber and field experiments were conducted. The researchers evaluated four important types of paint: (1) house paints (acrylic latex and oil-based); (2) a urea-alkyd coil coating; (3) a nitrocellulose-acrylic automotive refinishing paint; and (4) an alkyd industrial maintenance coating. In the chamber studies, paints were exposed to five separate controlled environmental conditions; (1) clean air; (2) sulfur dioxide at 262 $\mu g/m^3$ (0.1 ppm); (3) sulfur dioxide at 2620 $\mu g/m^3$ (1.0 ppm); (4) ozone at 196 $\mu g/m^3$ (0.1 ppm); and (5) ozone at 1960 $\mu g/m^3$ (1.0 ppm). The exposure chamber operated on a 2-hour light-dew cycle consisting of 1 hour of xenon light at 70 percent relative humidity and a black panel temperature of 66°C, followed by 1 hour of darkness at 100 percent relative humidity and 49°C during which period moisture condensed on the coated panels. To assess the influence of simulated sunlight, one group of panels was exposed to the light cycle while a like group of panels were exposed shaded from light during the entire exposure period. Erosion measurements were made after exposure periods of 400, 700, and 1000 hours; erosion rates were then calculated.

Generally, exposures to 2620 $\mu g/m^3$ (1 ppm) sulfur dioxide or 1960 $\mu g/m^3$ (1 ppm) ozone produced statistically significant erosion rate increases compared to clean air (zero pollution) conditions. Erosion rate increases, however, varied considerably among paint types. Oil-based house paint experienced the largest erosion rate increases, latex and coil coatings moderate increases, and the industiral maintenance coating and automotive refinish the smallest increases. Exposures to sulfur dioxide produced higher erosion rates than ozone for three of the paints; however, of more importance was that sulfur dioxide produced much larger erosion rate increases than ozone. Unshaded panels eroded more than shaded panels. Table 1-4 presents erosion rate data for the unshaded exposures. Exposures to 0.1 ppm pollutants did not produce significant erosion rate increases over clean air exposures.

TABLE 1-4. PAINT EROSION RATES AND T-TEST PROBABILITY DATA

PAINT EROSION RATES AND PROBABILITY DATA (T-TEST)
FOR CONTROLLED ENVIRONMENTAL LABORATORY EXPOSURES

	Mean erosion rate (nm/hour with 95-percent confidence limits) for unshaded panels		
Type of paint	Clean air control	SO_2 (1.0 ppm)	O_3 (1.0 ppm)
House paint			
oil	5.11 ± 1.8	[b]35.8 ± 4.83	[b]11.35 ± 2.67
latex	0.89 ± 0.38	[b]2.82 ± 0.25	[a]2.16 ± 1.50
Coil coating	3.02 ± .58	[b]8.66 ± 1.19	[a]3.78 ± 0.64
Automotive refinish	0.46 ± 0.02	0.79 ± 0.66	[b]1.30 ± 0.33
Industrial maintenance	4.72 ± 1.30	5.69 ± 1.78	7.14 ± 3.56

[a] Significantly different from control at an α of 0.05.

[b] Significantly different from control at an α of 0.01.

Source: Adapted from Yocom and Upham (1977).

Field exposures were conducted at four locations with different environments: (1) rural--clean air, (2) surburban, (3) urban--sulfur dioxide-dominant (annual mean level 60 μg/m^3), (4) and urban--oxidant-dominant (annual mean ozone level 40 μg/m^3). Panels were exposed facing both north and south, and were evaluated after 3, 7, and 14 months exposure. Table 1-5 shows the erosion rate results for the various coatings exposed facing south. In most cases, southern exposures produced somewhat larger erosion rates; this agrees with the unshaded versus shaded results of the laboratory study. Oil-based house paint again experienced by far the largest erosion rate increases,

TABLE 1-5. PAINT EROSION RATES AND T-TEST PROBABILITY DATA

PAINT EROSION RATES AND PROBABILITY DATA (T-TEST)
FOR FIELD EXPOSURES

	Mean erosion rate (nm/month with 95-percent confidence limits) for panels facing south			
Type of paint	Rural (clean air)	Suburban	Urban (SO_2 dominant, ~60 μg/m^3)	Urban (oxidant dominant, ~40 μg/m^3)
House paint				
oil	109 ± 191	[b]376 ± 124	[a]361 ± 124	[b]533 ± 157
latex	46 ± 13	[b]76 ± 18	[a]97 ± 8	165 ± 142
Coil coating	53 ± 20	[b]254 ± 48	[b]241 ± 20	[b]223 ± 43
Automotive refinish	23 ± 28	[a]58 ± 18	41 ± 10	43 ± 10
Industrial maintenance	91 ± 41	[a]208 ± 361	168 ± 99	[b]198 ± 61

[a] Significantly different from control at an α of 0.05.

[b] Significantly different from control at an α of 0.01.

Source: Adapted from Yocom and Upham (1977).

followed in order by the coil coating, latex house paint, industrial maintenance paint, and automotive refinish. Generally, the oxidant-dominant environment was more damaging than the sulfur dioxide dominant environment. It is noteworthy that the oil-based house paint and coil coating experienced the largest erosion rate increases in both the field and laboratory sulfur dioxide exposures. These coatings were the only ones that contained a calcium carbonate extender--a substance that is sensitive to attack by acids.

Spence et al. (1975) summarized the result of paint exposure to several gaseous pollutants from the full scale chamber studies reported by Haynie et al. and discussed earlier in relation to metal exposures. Four classes of painted surfaces were evaluated: oil base house paint, vinyl-acrylic latex house paint, vinyl coil coating, and acrylic coil coating. Significant questions can be raised as to how well the dew/light and temperature cycle and constant levels of SO_2 represent real life ambient exposure; however, they found a strong correlation between paint erosion for the oil base house paint and SO_2 and humidity. The vinyl and acrylic coil coating were unaffected, but aluminum corrosion caused blistering of the permiable latex house paint.

A multiple linear regression relationship was developed for the joint influence of SO_2 and relative humidity on the oil-base house paint:

$$E = 14.3 + 0.0151\ SO_2 + 0.388\ RH$$

where

E = erosion rate of μm/year
SO_2 = concentration of SO_2 in $\mu g/m^3$, and
RH = relative humidity in percent

This relationship indicates that paint erosion is significantly more sensitive to changes in humidity than SO_2. If we take the same hypothetical values used in testing the steel corrosion function discussed earlier (80 and

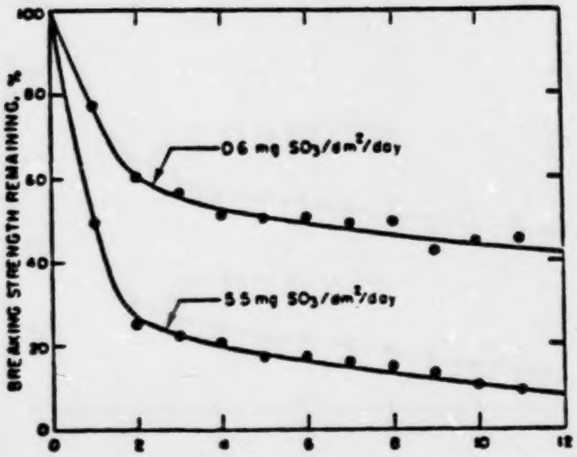
160 $\mu g/m^3$ of SO_2 at 55 percent RH, and 55 and 65 percent RH at 100 $\mu g/m^3$ SO_2), we find that the large change in SO_2 will produce a 3 percent change in erosion and the moderate change in RH will produce a 10 percent change in erosion.

The present understanding of damage to paint from air pollution is based primarily upon two sets of chamber studies and one set of field exposures. Since the field studies were carried out in the early 1970s, there is a need for further laboratory and field studies to determine the importance of paint damage from present day levels of sulfur oxides. Furthermore, these studies should include present day formulations (especially water-based paints) that may have a different response to air pollutants than those used earlier.

1.2.4 Textiles

Sulfur oxides are capable of weakening natural and some synthetic fibers. Cotton and its relative, viscose rayon, are cellulose fibers and can be weakened by SO_2 by breakage of the cellulose chain at the glucoside linkage. Polyamides such as Nylons 6 and 66 can be weakened by SO_2 and acid sulfate aerosols, especially when such fibers are small in diameter and under tension. Polyester, acrylic, and polypropylene fibers are resistant to SO_2 damage, but certain of these fibers may be susceptible to damage from acidic particles containing sulfates.

Brysson and co-workers (1967) exposed cotton fabrics to the outdoor atmosphere for 1 year at several sites in St. Louis, Missouri, and Chicago, Illinois. Individual samples were removed from the exposure rack each month. Sulfur oxide concentrations were estimated by means of lead peroxide sulfation plates. In a review of the Brysson et al. (1967) study, Upham and Salvin (1975) reported a correlation coefficient of 0.95 for breaking strength versus sulfation for cotton duck cloth. Figure 1-4 shows the effect of exposure time



EXPOSURE, months

FIGURE 1-4. Effects of sulfation and time on tensile strength of cotton duck. Source: Brysson et al., 1967.

on the relative breaking strength of cotton duck at two levels of average sulfation rate.

Zeronian (1970) carried out laboratory exposures in which he exposed cotton and rayon fabrics for 7 days to clean air with and without 250 $\mu g/m^3$ (0.1 ppm) sulfur dioxide. Both controlled environments included continuous exposure to artificial light (xenon arc) and a water spray turned on for 18 minutes every two hours. Loss in strength for all fabrics exposed to clean air averaged 13 percent, while the fabrics exposed to air containing sulfur dioxide averaged 21 percent. Zeronian et al. (1971) also exposed fabrics made from manmade fibers--nylon, polyester, and modacrylic--to controlled environmental conditions similar to the cotton exposures, except that the sulfur dioxide level was 486 $\mu g/m^3$ (0.2 ppm). He found that only the nylon fabrics were affected, losing 80 percent of their strength when exposed to sulfur dioxide and only 40 percent when exposed in clean air.

While it has been clearly demonstrated that SO_2 can damage some textiles, there are some fundamental questions on the current relative importance of this potential problem in relation to other air pollution material effects problems:

1. How much susceptible material is still in use in outdoor exposures? To what extent have coated fabrics and more resistant synthetic fabrics supplanted such fabrics as cotton duck?
2. Textiles spend most of their useful life indoors where SO_2 concentrations are generally less than half of those outdoors.
3. Outdoor levels of SO_2 in urban areas have been reduced drastically from those levels that existed in the early

1960s in cities like St. Louis and Chicago where several material damage studies have been carried out.

4. Products made of textiles (clothing, draperies, etc.) tend to be replaced long before air pollution has a significant effect on useful life.

These questions must be addressed before further research is carried out on the effect of air pollutants on textiles.

1.2.5 Building Materials and Works of Art

Sulfur oxides are involved in the deterioration of several types of building materials. The importance of this damage is partly a problem of loss in structural integrity, but more important is the destruction and disfigurement of buildings, monuments and other structures and articles of great historical and artistic value. Such damage transcends the mundane consideration of replacement value of articles and surfaces used in our everyday lives. The damage to priceless buildings and works of art is not nearly the problem in the United States that it is in Europe and parts of Asia because there are few buildings over 200 to 300 years old here. Americans have a tendency to demolish buildings that are thought to have outlived their usefulness. However, more and more old buildings are now being preserved as a result of high construction costs and an increased interest in our architectural and historical heritage. This trend will place increased importance on the effects of air pollution on older material surfaces.

Air pollution damage to the buildings and monuments on the Acropolis is one of the most serious and widely publicized air pollution damage situations in the world and has been the subject of several international conferences (International Meeting, 1977, and Proceedings of the Second International Symposium, 1976). Yocom (1979) has summarized the air pollution-related damage to buildings on the Acropolis in terms of four problems:

1. Sooty encrustation of gypsum in protected areas from the reaction between marble and sulfur oxides.
2. Loss of surface detail in areas exposed to the weather from the dissolution of gypsum.
3. Cracking of joints repaired earlier by means of iron pins which have corroded and expanded. This corrosion is thought to have accelerated as a result of sulfur oxides.
4. Threatened collapse of the Porch of the Caryatids on the Erechthion because the steel member installed about 1900 to support the roof is badly corroded.

Similar cases have been reported elsewhere. The Coliseum and Arch of Titus in Rome, Italy, and the San Marco Basilica in Venice, Italy, all show accelerated decay attributable to air pollution. The situation in Florence, Italy, is described as disastrous. In France, conservation specialists have removed statues from the exterior of cathedrals and replaced them with copies. A team of experts has been fighting decay and corrosion destroying the massive, twin-spired Cologne Cathedral, the most magnificant church building of the German high gothic era of around 1200 A.D. Polluted atmospheres are threatening centuries-old shrines, temples, and buildings in highly industrial areas of Japan. Cleopatra's Needle, the large stone obelisk moved from Alexandria, Egypt, to London, England, has suffered more deterioration in the atmosphere of London in 85 years than in the earlier 3000 or more years of its history. Another ancient Egyptian obelisk standing in Central Park in New York City, New York, shows similar decay.

The protection and repair of the old buildings and cathedrals of England has been thoroughly discussed by several authors (Feilen, 1975 and Schaffer, 1957). Aside from air pollution, severe damage is caused by vibrations from vehicular traffic which accelerate damage from pollutants and weathering from natural causes; for example, freezing and thawing.

Sulfur consuming bacteria may also be directly or indirectly responsible for a significant amount of stone damage. Hansen (1980), in summarizing the work of Curri in Italy, points out that the microbe, Thiobacillus thioparus, one of several sulfur utilizing organisms, can attack carbonate stone, converting the calcium carbonate to calcium sulfate (gypsum). Zajik (1969), gives the exothermic reaction: $S + 1.5\ O_2 + Ca\ CO_3 \quad CA\ SO_4 + CO_2$. One method proposed to stop this type of attack is to treat the surface with an antibiotic or bactericide.

Longinelli and Bartelloni (1978) have carried out research on damage to building stone in Venice, Italy. In their work they used isotopic analysis of O, S, and C in rainwater and stone to show that damage to buildings, which has been most severe since 1900, to be caused primarily by sulfur-bearing air pollutants. In spite of the proximity of Venice to the sea, sea water spray and aerosols play only a minor role in this deterioration.

At a recent NAS conference on conservation of historic stone monuments and buildings, Tombach (1981) summarized mechanisms contributing to stone decay (see Table 1-6). While more information on these mechanisms is becoming available, definitive quantification of the relative contribution of ambient SO_2 to deterioration of the various types of stone is not available.

Glass or ceramic surfaces are thought to be impervious to damage from all air pollutants except perhaps fluorides. However, it has been found that certain types of medieval glass used in stained glass windows were made with potash derived from woodashes because the medieval artisans were isolated from the sources of soda ash (Chemical Week, 1979). The potassium salts in such

TABLE 1-6. MECHANISMS CONTRIBUTING TO STONE DECAY. PRINCIPAL ATMOSPHERIC FACTORS PARTICIPATING THESE MECHANISMS ARE DENOTED BY SOLID CIRCLES: SECONDARY FACTORS ARE INDICATED BY OPEN CIRCLES

Mechanism	Rainfall	Fog	Humidity	Temperature	Solar Insolation	Wind	Gaseous Pollutants	Aerosol
A. External Abrasion								
1. Erosion by windborne particles						●		●
2. Erosion by rainfall	●							
3. Erosion by surface ice	●	●		●				
B. Volume Change of Stone								
1. Differential expansion of mineral grains				●			0	
2. Differential bulk expansion due to uneven heating				●	●			
3. Differential expansion of differing materials at joints				●				
C. Volume Change of Material in Capillaries and Interstices								
1. Freezing of water	●	●		●				
2. Expansion of water when heated by sun	●	●		●	●			
3. Trapping of water under pressure when surface freezes	●	●		●				
4. Swelling of water-imbibing minerals by osmotic pressure	●	●	●				0	0
5. Hydration of efflorescences, internal impurities, and stone constituents	●		●				0	0
6. Crystallization of salts			●	●	●	●	0	0
7. Oxidation of materials into more-voluminous forms	●	●					0	
D. Dissolution of Stone or Change of Chemical Form								
1. Dissolution in rain water	●			●			●	●
2. Dissolution by acids formed on stone by atmospheric gases or particles and water	●	●	●	●			●	●
3. Reaction of stone with SO_2 to form water-soluble material	●	●		●			●	
4. Reaction of stone with acidic clay aerosol particles	●	●		●				●
E. Biological Activity								
1. Chemical attack by chelating, nitrifying, sulfur-reducing, or sulfur-oxidizing bacteria			●	●			●	
2. Erosion by symbiotic assemblages and higher plants which penetrate stone or produce damaging excretions	0	0	●	●				

Source: Tombach (1981).

glass are more soluble than sodium salts, and the glass surface simply leaches away.

Because of the importance of air pollution damage to priceless and irreplaceable buildings, monuments and works of art, there is an urgent need for a well-conceived, integrated research effort covering a broad front to attack this problem. The elements include but are not limited to:

- Identification of damage mechanism and the specific pollutants and other environmental effects responsible for damage.
- Strategies for air quality control.
- Methods of protection and/or isolation to retard damage.
- Methods of restoration.

1.2.6 Other Effects of Sulfur Oxides

Sulfur oxides are capable of damaging a number of other materials or material systems. However, the importance of these effects is much less than those discussed above.

1.2.6.1 Leather--Sulfur oxides cause leather to lose much of its strength and ultimately to disintegrate. As early as 1843, Faraday came to the conclusion that the rotting of leather upholstery on chairs in a London club was the direct result of sulfur compounds in the air (Yocom and Upham, 1977). Spedding et al. (1971) reported that the controlling factor in SO_2 uptake is the rate of SO_2 diffusion to the leather surface. The formation of H_2SO_4 in the presence of water is followed by hydrolysis of the protein (collagen) of which leather is principally composed. This weakening of leather causes cracking and ultimately results in reduction of the leather to a red-brown powder (Spedding et al., 1971; Yocom and Grappone, 1976).

The destruction of leather by absorption of SO_2 has long been known and was described in detail by Prenderleith (1957). The buildup of H_2SO_4 in aged leathers correlates with deterioration, which can be reduced by inactivating the SO_4^{2-} ion and by pH buffering. Deterioration of leather is important in bookbinding and in leather upholstery. The use of artificial leathers has reduced damage costs, though the storage of leather-bound books in libraries can pose a serious problem.

1.2.6.2 Paper--Paper made prior to about 1750 is not seriously damaged by sulfur dioxide. This date is about the point in history when chemical methods for papermaking were introduced. Apparently, the small amounts of metallic impurities in "modern" paper accelerate the conversion, in the presence of moisture, of absorbed sulfur dioxide to sulfuric acid (Spedding et al. 1971). In any event, paper is essentially cellulose and can be hydrolyzed by acids. The ultimate effect on paper is to make it more brittle.

Although most paper is used in objects with a short service-life, and steps have been taken to improve the acid resistance of books, the preservation of documents is of concern in museums and archives. Coating paper with polymers impervious to gases is an established process. It is estimated that 50 percent of the books printed between 1900 and 1940 are in need of conservation. The New York Public Library conserves old books by microfilming, lamination, and electrostatic reproduction (Kingery, 1960). The library spent $900,000 between 1952 and 1967 to microfilm books that had deteriorated (Waddell, 1974).

1.2.6.3 Electrical Contacts--Gaseous and particulate pollutants have been a source of trouble to the electronics industry. Low power electrical contacts such as those used in computers and sophisticated instrumentation are especially susceptible. Copper and silver contacts are susceptible to sulfur containing gases (SO_2 and H_2S) through the production of sulfides and/or oxides on the contact surface, thus producing an increase in electrical resistance.

This problem has been reduced in severity through plating the contact surface with precious metals, providing air purification systems for the atmosphere surrounding the electronic equipment, and through the reduction of ambient air pollution levels.

1.3 PARTICULATE MATTER

The primary effect of particulate matter on materials is the soiling of surfaces. However, like sulfur oxides, particulate matter, under the proper conditions, can enhance surface damage particularly in serving as centers for condensation of moisture and adsorption of gaseous pollutants. While soiling itself does not necessarily create direct damage, removal of the particulate matter by cleaning can increase wear and shorten the life of the article being cleaned.

If it is difficult to isolate sulfur oxide damage from the environmental effects, it is far more difficult to isolate the specific influence of particulate matter. There are several reasons for this:

- High levels of sulfur oxides and particulate matter tend to coexist.
- Particles offer surfaces for the adsorption of gaseous pollutants. Thus damage appearing to be related to a particle may be the result of adsorbed gaseous pollutants.
- SO_2 converts to sulfates in the atmosphere and on surfaces. Such secondary sulfates are in particulate form, but are more related to atmospheric SO_2 than particulate matter.

1.3.1 Corrosion of Metals

Some of the experiments of Vernon (1935) showed that moist air polluted with SO_2 and particles of charcoal produced corrosion much more rapidly than air containing SO_2 and moisture alone. He reasoned that the effect of the particles was primarily physical in that they increased the concentration of SO_2 by adsorption and created "hot spots" of SO_2 concentration. Sanyal and

Singhania (1956) stated that particulate matter had a "profound" effect on corrosion rates. They believed that the influence of particulate matter on corrosion was related to its electrolytic, hygroscopic and/or acidic properties, and its ability to absorb corrosive pollutant gases.

While these laboratory studies appear to show a strong influence of suspended particulate matter with corrosion, field studies have not confirmed this effect. However, as pointed out in Section 1.2.2.3, the differences in SO_2 damage functions for zinc and galvanized steel based on air quality/corrosion data between the early 1960's and mid 1970's may reflect in part differences in particulate matter levels between the two periods.

1.3.2 Building Materials

The primary effect of particulate matter on building materials is soiling. Thus the ultimate impact is aesthetic rather than a loss in physical strength or integrity. Dark particulate matter largely from combustion sources has blackened buildings in many urban areas of the world. Beloin and Haynie (1975) developed dose-response relationships for suspended PM and soiling of various building materials. They compared the rates of soiling by different levels of TSP on six different building materials over 2 years. The mean annual PM concentrations at the five study sites ranged from 60 $\mu g/m^3$ for a rural residential location to 250 $\mu g/m^3$ for an industrial residential environment. The exposed materials included painted cedar siding, concrete block, brick, limestone, asphalt shingles, and window glass. Table 1-7 shows the results of regression for soiling of building materials as a function of TSP dose.

It is often claimed that particulate matter deposits on stone surfaces carry acids and soluble salts to the surface thereby causing chemical damage. On the other hand, Riederer (1973) believes that air pollutants including

TABLE 1-7. RESULTS OF REGRESSION FOR SOILING OF BUILDING MATERIALS AS A FUNCTION OF TSP DOSE

Material	N	A	B	S_A^2	S_B^2	S_E^2	R^2
Oil base paint	400	89.43	-0.2768	0.0641	0.000069	7.6510	0.745
Tint base paint	400	86.13	-0.2618	0.0571	0.000061	6.8265	0.738
Sheltered acrylic emulsion paint	400	91.54	-0.593	0.1156	0.000123	13.8143	0.880
Acrylic emulsion paint	720	90.79	-0.4131	0.0497	0.000026	8.3791	0.902
Shingles	48	43.50	-0.199	0.5771	0.000258	7.6992	0.769
Concrete	160	41.75	-0.0458	0.1338	0.000080	7.5011	0.143
Coated limestone	80	44.57	+0.0779	0.2464	0.000164	6.9046	0.347
Uncoated limestone	80	46.99	-0.0503	0.1500	0.000089	4.2035	0.266
Coated red brick	80	12.95	-0.0296	0.0223	0.000013	0.6255	0.459
Uncoated red brick	80	14.88	-0.0374	0.0331	0.000020	0.9274	0.477
Coated yellow brick	80	45.05	-0.1133	0.5337	0.000317	14.9533	0.342
Uncoated yellow brick	80	43.21	-0.1133	0.2740	0.000168	7.6773	0.503
Glass	45	0.2806	+0.0314	0.008077	0.000007	0.6851	0.340

Note: Equation used in this regression analysis was reflectance = $B(\text{TSP x months of exposure})^{\frac{1}{2}} + A$,

except in the case of shingles, where reflectance = $\frac{B(\text{TSP-x-months of exposure})}{10} + A$

N, = Number of data sets (dependent upon the number of controlled variables in the factorial experiment).

A, = Intercept of linear regression.

B, = Slope of linear regression.

S_A^2, = Estimated variance of intercept.

S_B^2, = Estimated variance of slope.

S_E^2, = Residual variance (error).

R^2, = Correlation index (fraction of variability accounted for by regression).

TSP = Total suspended particulate matter in $\mu g/m^3$.

Source: Abstracted from Beloin and Haynie, 1975.

particulate matter have little effect on building stone. He believes that the sooty encrustations of gypsum and organic material do not chemically involve the underlying stone. This is contradicted by Gauri and Holdren (1981) and many others, although the attribution of damage is more to SO_2 than particulate matter or other pollutants.

Recent examination by scanning electron microscopy (SEM) of exposed marble from several locations in northern Italy provides evidence of a major role for carbonaceous particles in marble deterioration. Del Monte et al. (1981) report that SEM morphological characterization, together with particle analysis by X-ray diffraction and X-ray energy dispersive analyzer data, identifies the majority of the carbonaceous particles as products of oil fired boiler/combusion. Particle median diameter was ~ 10 μm. Del Monte et al. also presented evidence strongly suggesting that the carbonaceous particles are very important in oxidizing SO_2 to SO_4^{2-}. If further research substantiates this finding, current understanding of the relative roles of SO_2 and PM in marble deterioration might well be substantially modified.

1.3.3 Paints

As in the case of building materials, the primary effect of particulate matter on paint is soiling. Soluble salts such as iron sulfate contained in deposited particles can also produce staining.

Chemically active large particles such as acid smut from oil-fired boilers, or mortar dust near building demolition sites can severely damage automotive paint (Exley, 1970; Fochtman and Langer, 1957). The effects range from discoloration of the paint film to ultimate penetration of the paint film and corrosion of the underlying metal in the vicinity of individual particles. Large particles becoming imbedded in a freshly painted surface can act as wicks to transfer moisture and corrosive pollutants such as SO_2 to the underlying material surface (Cowling and Roberts, 1954).

1.3.4 Fabrics

Large particles imbedded in fabrics are capable of causing physical damage to fabrics that receive considerable flexing (Yocom and McCaldin, 1979). Soiling from particulate matter does not normally cause direct damage to fabrics, but increased cleaning frequency reduces the service life of articles made of fabric. However, the stresses of the natural environment sunlight and water vapor, and gaseous pollutants such as NO_2, ozone and SO_2 are much more important than those related to particulate matter (National Research Council, 1979). Furthermore, articles made of fabric (clothes, curtains, rugs, upholstered furniture, bedding, etc.) tend mostly to be indoors where levels of particulate matter and other pollutants may be lower than those out of doors. Therefore, the extent of physical damage to fabrics from outdoor levels of particulate matter are especially difficult to assess. Furthermore, new, more resistant fabrics and fabric treatment or coating processes have tended to minimize the deleterious effects of particulate matter on fabrics.

1.4 NITROGEN OXIDES

It has been demonstrated that nitrogen oxides (principally NO_2) are capable of damaging several types of materials. The most significant effect is on certain types of fabric dyes. NO_2 is also involved in the weakening of some fabrics, causing deterioration of certain types of plastic materials, and in the corrosion of metals.

The ability of NO_2 to be converted into nitrates in the atmosphere is part of the "acidic deposition" or "acid rain" problem. While elevated levels of nitrates are often found in acidic rain water, the relative importance of anthropogenic nitrogen oxides in any material damage caused by acidic rain (e.g., metal corrosion, or stone damage) is not known. It is probable that any such indirect effect of nitrogen oxides is small in comparison with effects related to sulfur oxides, since only at low levels of SO_x and high levels of NO_x is the formation of metal nitrates thermodynamically favored.

To put the role of nitrogen oxides in damaging fabrics and fabric dyes in perspective, these materials usually spend most of their useful lives in the indoor environment where levels of NO_2 are quite different from those outdoors. In homes or other structures with no sources of NO_2 (e.g., gas-fired cooking stoves) indoor levels are invariably less than those outdoors. Yocom et al. (1977) showed that concentrations of NO_2 inside homes with gas cooking stoves can be several times outdoor concentrations, but that the concentration gradient from the kitchen near the sources to other parts of the house is extremely steep because of the short half life of NO_2 in homes. In warehouses where fabric and clothing are stored, indoor levels of NO_2 would be elevated where unvented heaters and combustion powered fork-lift trucks are used.

Another aspect of defining the real life exposure of fabric, and especially clothing, to oxides of nitrogen relates to use of chamber studies to establish the exposure/effect relationship. Chamber studies show the relationship between material effects to exposures without the complicating influence of other pollutants and wide variations in other environmental factors such as temperature and humidity. Chamber exposures are generally carried out as dynamic systems where concentrations are maintained by adding known amounts of the pollutant gas to a moving air stream which is maintained at predetermined temperature and humidity conditions with or without the exposure to simulated sunlight. A serious question arises as to the meaning of chamber study data when applied to real life exposures, particularly indoor exposures most pertinent to these materials. Indoor exposures tend to be quite static (that is, where there is little or no replenishment of the NO_2). An example of a static exposure is a closet where fabrics in the form of clothing are stored for long periods of time. If one further considers closet storage where there is a large surface area for adsorption or absorption of NO_2, one would expect the concentrations to which clothing is exposed to be a very small fraction of the concentrations existing in the house as a whole. Furthermore, assuming no sources of NO_2 inside the house, the general indoor concentration would be expected to be a small fraction of that outdoors. Thus, in this scenario the outdoor concentration bears little resemblance to the concentration regime to which the materials are being exposed, and chamber studies designed to determine the effects of a pollutant or material in which the presumed outdoor concentrations are being depicted tend to be misleading.

1.4.1 Dyed Fabrics

The fading of textile dyes by air pollutants, primarily nitrogen dioxide and ozone, has been a particularly vexing problem for the textile industry during much of the twentieth century. The problem first surfaced just prior to World War I, when a German dye manufacturer investigated some unusual cases of fading of stored woolen goods (Giles, 1965). The cause was traced to nitrogen oxides in the air produced by open electric-arc lamps and incandescent gas mantles. All the susceptible dyes contained free or substituted amino groups.

In subsequent years, increased replacement of older forms of lighting with electric filament lamps led to a general decline of the wool-fading problem. In the mid-1920's, however, a newly developed manmade fiber, cellulose acetate rayon, was introduced. Since traditional dyes were of little use on this fiber, chemists developed an entirely new line of dyestuffs called disperse dyes. Many are derived from anthraquinone and therefore contain amino groups. Shortly thereafter, a puzzling type of fading began to show up on blue, green, and violet shades of dyed acetate goods. This mysterious fading was called "gas fading" because it was frequently observed in rooms heated by gas heaters.

During the 1930's, acetate fading became a serious problem. Dye and fiber chemists, apparently unaware of the earlier German work, devoted considerable efforts toward a solution. These efforts culminated in 1937 when Rowe and Chamberlain (1937) systematically investigated the fundamental chemistry of dye degradation and independently reached the same conclusions as the earlier German team. Since then, much research has been carried out in an effort to understand gas fading and to develop ways of preventing it. Upham and Salvin (1975) have summarized much of the information on this subject up to 1975.

The ability of a fiber to absorb NO_2 plays an important role in dye fading mechanism. For example, Salvin (1952) showed that cellulose acetate is an excellent absorber of NO_2. Polyester and polyacrylic fibers have low absorption rates for NO_2. Nylon, cotton, viscose rayon and wool have intermediate rates.

Table 1-8, based on a compilation prepared by U.S. Environmental Protection Agency (1979) in the Draft Air Quality Criteria Document for Nitrogen Oxides, shows the results of both chamber and field tests of dye fading on cellulose acetate and cellulosics (cotton and rayon).

The American Association of Textile Chemist and Colorists (AATCC), (Salvin, 1964), exposed a wide range of fibers and dyes to the atmosphere of four U.S. cities representing different air quality and meteorological regimes. Exposures were made in cabinets to isolate the samples from sunlight. Air quality was monitored for SO_2, NO_x, and O_3. Fading was demonstrated on a

TABLE 1-8. FADING OF DYES ON CELLULOSE ACETATE AND CELLULOSICS (COTTON AND RAYON) BY NITROGEN DIOXIDE (U.S. EPA, 1979)

Dyed Fibers	Exposure	Pollutant	Concentration of Pollutant		Time	Effect	Reference
			μg/m³	ppm			
Acetate	Gas heated rooms	NO_2	3,760	2.0	N/A	Fading	Rowe and Chamberlain, 1937
Acetate	Chamber	NO_2	3,760	2.0	16 hr	Fading	Seibert, 1940
Acetate	Pittsburgh-urban, Ames-rural	NO_2-O_3	N/A		6 mo	Fading	Salvin and Walker, 1955
Acetate	Chamber	NO_2	3,760	2.0	16 hr	Fading	Salvin, et al., 1952
Cotton-Rayon	Clothes dryer	NO_2	1,128-3,760	0.6-2.0	1 hr cycle	Fading	McLendon and Richardson, 1965
Acetate-Cotton, Rayon	Los Angeles	NO_2 + O_3 + SO_2	489 + 312 + 131	0.26 + 0.21 + 0.05	30 to 120 days	Fading	Salvin, 1964
	Chicago	NO_2 + O_3 + SO_2	414 + 10 + 655	0.22 + 0.005 + 0.25			
Cotton-Rayon	Chamber	SO_2-NO_2	3,760	2.0	16 hr	Fading	Salvin, 1969
Cotton-Rayon	Chamber	SO_2-NO_2 and O_3	N/A		54 hr	Fading	Ajax et al., 1967

TABLE 1-8 (Continued).

Dyed Fibers	Exposure	Pollutant	Concentration of Pollutant $\mu g/m^3$	ppm	Time	Effect	Reference
Range of Fibers	Field-Urban, Rural	SO_2-NO_2+O_3	N/A		24 mo	Fading	Beloin, 1972
Range of Fibers	Chamber	NO_2	94-940	0.05-0.5	12 wk	Fading	Beloin, 1973
Range of Fibers	Chamber	NO_2 + Xenon arc radiation	940	0.5	10 to 80 hr	Fading	Hemphill et al., 1976
Acetate-Cotton, Rayon	Chamber	NO_2	94-940	0.05-0.5	N/A	Fading	Upham et al., 1976
Acetate-Cotton, Rayon	Survey	NO_2, SO_2, H_2S	Service Complaints		N/A	Fading	Upham and Salvin, 1975

range of fabrics including cotton and rayons, and several types of dyes (vat, sulfur and fiber-reactive) applicable to cellulosics exhibited color change. However, the results were not able to show the degree of responsibility for each of the pollutants in the effects noted.

In an expansion of the AATCC field program Beloin (1972) exposed 67 dye-fabric combinations, using 56 dyes, at 11 urban and rural sites in the United States. As in the case of the AATCC works, the fabric samples were exposed in covered, louvered cabinets to exclude light, and ambient levels of SO_2, NO_x and O_3 were monitored. Urban sites produced more fading than rural sites. Fading also increased with both temperature and humidity. The data did not show the effect of specific pollutants, but statistical analysis identified NO_2 concentrations as a significant variable.

Beloin (1973) also carried out a laboratory study in which 20 dyed fabrics were exposed to individual pollutants (SO_2, NO, NO_2 and O_3) at two levels of concentration, relative humidity and temperature. Severe fading occurred at high humidity and temperature (90 percent RH and 32°C) and high NO_2 level (940 $\mu g/m^3$) in eight of nine samples of cotton or viscose. Significant fading also occurred at high humidity and moderate NO_2 level (94 $\mu g/m^3$).

The above laboratory results were confirmed in chamber tests conducted by Upham et al. (1976).

Dyed nylon fabrics are also susceptible to fading in polluted atmospheres but are not as sensitive in this respect as cotton, rayon, and cellulose acetate. Dyed polyester fabrics are more resistant to NO_2 damage than nylon. Table 1-9 is a summary by U.S. Environmental Protection Agency (1978) of the work of several researchers on field and laboratory exposures of dyed nylon and polyester fabrics to NO_2. Field exposure of a range of dyes on nylon to urban atmospheres containing NO_2, SO_2 and O_3 produced significant dye fading. Dyed polyester fabrics were unaffected.

TABLE 1-9. EFFECT OF NITROGEN DIOXIDE ON FADING OF DYES ON NYLON AND POLYESTER (U.S. EPA, 1978)

Dyed Fibers	Exposure	Pollutant	Concentration of Pollutant		Time	Effect	Reference
			$\mu g/m^3$	ppm			
Nylon	Chicago Los Angeles	NO_2, SO_2, O_3	188 282	0.1 0.15	30 to 120 days 30 to 120 days	Fading	Salvin, 1964
Polyester	Chicago Los Angeles	NO_2, SO_2, O_3	376 282	0.2 0.15	30 to 120 days 30 to 120 days	Unchanged	Ibid.
Nylon	Urban Sites	NO_2, SO_2, O_3	376	0.2	3 to 24 months	Fading	Belion, 1972
Poylester	Urban Sites	NO_2, SO_2, O_3	376	0.2	3 to 24 months	Unchanged	Ibid.
Nylon	Chamber High Humidity	NO_2	188 to 1,880	0.1 to 1	12 weeks	Fading	Belion, 1973
Polyester	Chamber High Humidity	NO_2	188 to 1,880	0.1 to 1	12 weeks	Unchanges	Ibid.
Nylon	Chamber High Humidity	NO_2	376	0.2	48 hours	Fading	Imperial Chemical Industires
Nylon	Chamber High Humidity Xenon Arc	NO_2	940	0.5	30 to 120 hrs	More fading than without NO_2	Hemphill, 1976
Polyester Permanent Press	Chamber	NO_2	940	0.5	16 hours	Fading	Salvin, 1966
Polyester Textured Double Knit	Chamber	NO2	940	0.5	16 hours	Fading	Urbanik, 1974

The fading of permanent press and double-knit polyester in chamber tests (see Table 1-9; Urbanik, 1974; Morris, 1966) does not occur in the fiber matrix. Dye which migrates into the surface resins and surfactants applied to these fabrics during manufacture is affected by NO_2.

In addition to dye fading, a number of workers have shown that NO_2 can be responsible for yellowing of white fabrics. Such yellowing is often exacerbated by fabric whiteners, softeners, and static compounds and other surface treatment materials. The results of this work have been summarized by U.S. Environmental Protection Agency (1978).

1.4.2 Loss of Fiber Strength

Nitrogen oxides (especially NO_2) like sulfur oxides are capable of weakening cellulose and nylon fibers by acid hydrolysis. However, the question must be asked as to how important this effect is in view of the predominant use of fabrics indoors and the trend of using more resistant fabrics in the outdoor environment.

Field and laboratory studies of the effects of nitrogen oxides on fiber strength are somewhat inconclusive. One chamber study by Morris (1966) exposed cotton samples in two chambers to sunlight, but the air for one chamber was filtered through activated carbon which presumably removed NO_2, O_3, SO_2 and other pollutants. Since the study was carried out in Berkeley, California, it was reasoned that little SO_2 was present and the principal gaseous pollutant in the ambient atmosphere was NO_2. Loss of fiber strength was greatest in the presence of unfiltered air and was attributed to the presence of NO_2.

The work of Zeronian (1971) was also inconclusive. He exposed various fibers to xenon arc radiation and air containing 376 $\mu g/m^3$ of NO_2 at several combinations of temperature and relative humidity. While considerable loss in strength occurred, the differential effect of NO_2 and radiation could not be isolated.

1.4.3 Effects on Plastics and Elastomers

The increased use of synthetic organic materials such as polyolefins, polyvinyl chloride, polyacrylonitrile, and polyamides in a variety of consumer and other manufactured products and the maintenance of their strength places some importance on the effects of air pollutants on these materials. Plastic and elastomeric materials are formulated to maximize aging properties. The "weathering" or aging of these materials is dominated by the effect of sunlight the importance of which is intensified by the increased use of plastics in automobiles.

Polymers representing the structures in plastics, as well as textiles, were exposed by Jellinek et al. (1969) to the action of SO_2, NO_2, and ozone. The polymers tested included polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyacrylonitrile, butyl rubber and nylon. All polymers suffered deterioration in strength. Butyl rubber was more susceptible to SO_2 and NO_2 than other polymers. However, the effect of O_3 on the rubber was more pronounced than that of the SO_2 or the NO_2.

Jellinek (1970) examined the reaction of linear polymers, including nylon and polypropylene, to NO_2 at concentrations of 1,880 to 9,400 $\mu g/m^3$. Nylon 66 suffered chain scission. (Chain scission produces polymers having lower molecular weights and lower strength.) Polypropylene tended to crosslink. Chain scission of polymers caused by small concentrations of SO_2 and NO_2 took place in the presence of air and UV radiation.

The action of NO_2 and O_3 on polyurethane also was investigated by Jellinek (1974). The tensile strength of linear polyurethane was reduced by NO_2 alone and also by NO_2 plus O_3. Chain scission resulting in lower molecular weights and formation of nitro- and nitroso-groups along the polymer backbone occurred upon exposure to NO_2.

1.4.4 Corrosion of Metals

Nitrogen oxides, as potentially acid pollutants, are implicated in several types of corrosion: pitting, selective leaching, and stress corrosion. However, their role in outdoor corrosion of metals is much less important than that of sulfur oxides. U.S. Environmental Protection Agency (1978) has summarized the principal research results on the effects of nitrogen oxides and nitrates on metals. Table 1-10 summarizes this work in qualitive terms.

Probably the most significant form of nitrogen oxides damage to metals is stress corrosion of non-ferrous springs where nitrate containing deposits appear to be implicated. Hermance and his associates (Hermance et al., 1971; McKinney and Hermance, 1967; Hermance, 1966) at Bell Telephone Laboratories have carried out a considerable research effort to better understand this problem which has caused failures in telephone switching equipment at various places in the U.S. An important finding of this work was that nitrate salts are more hygroscopic than chlorides or sulfate salts. Thus nitrate deposits may lower threshold humidity requirements for the production of electroyltic corrosion effects.

As was discussed in Section 1.2.1.3 Gerhard and Haynie (1974) pointed out the possible implication of acidic air pollution in the catastrophic failure of metals. The reference to this work in Table 1-10 is perhaps somewhat inappropriate, since they clearly emphasized sulfur oxides rather than nitrogen oxides.

1.5 OZONE

Ozone is an extremely reactive gas with the ability to react with many organic materials, both natural and manmade. Materials especially susceptible to ozone attack are elastomers (rubber), textile fibers and dyes, and some types of paints. While there are other strong oxidizing materials in polluted

TABLE 1-10. CORROSION OF METALS BY NITROGEN DIOXIDE
(U.S. EPA, 1978)

Metal	Exposure	Pollutant	Effect	Reference
Nickel Brass	Los Angeles	Nitrates	Strength loss	Hermance et al. 1971
Nickel Brass	Los Angeles	Nitrates	Strength loss	McKinney and Hermance, 1967
Nickel	Los Angeles New York	Nitrates	Corrosion	Hermance, 1966
Tungsten	Chamber	NO_2	Change oxide	Lazareva, 1973
Electric Contacts	Field	NO_2-SO_2-H_2S	Corrosion film	Chiaranzelli and Joba, 1966
Metal Parts	Field	NO_2-SO_2-O_3	Failure	Gerhard and Haynie, 1974

atmospheres, ozone is the most abundant of such active oxidants. Depending upon the structure of susceptible organic polymers, the effect of ozone is through chain-scission or cross-linking, or both. The first of these effects produces a reduction in molecular weight and decrease in tensile strength, while the second tends to increase the rigidity of some polymers making them more brittle and less resilient.

1.5.1 Elastomers

The aging of cracking of natural rubber has long been associated with exposure to the atmosphere and was originally thought to be the result of sunlight. Van Rossem and Talem (1931) showed that ozone, rather than sunlight, was the cause of rubber cracking from atmospheric exposure. In the 1940's and 50's it was recognized by a number of investigators (Norton, 1970; Newton, 1945; Crabtree and Biggs, 1953; Crabtree and Kemp, 1946) that in addition to ozone, other reactive species in atmospheres polluted with photochemical smog could produce rubber cracking. In work performed in the early days of the Los Angeles smog problem, Bradley and Haagen-Smit (1951) developed a method for measuring atmospheric ozone concentrations using stressed rubber samples and measuring crack depth at the end of specified exposure periods. For several years, this method was considered to be the most reliable and specific method for atmospheric ozone measurement.

The cracking of natural rubber is initiated by ozone attack at the double bond. Therefore synthetic elastomers such as, styrene-butadiene, polybutadiene, and polyisoprene are also susceptible to ozone damage. Elastomers with saturated chemical structures or which contain halogen atoms tend to be ozone-resistant.

Mueller and Stickney (1970) reviewed the physical and economic effects of air pollution on elastomers and discussed the development of rubber additives to combat ozone attack. These are generally aromatic amines and phenols. Such materials are widely used in rubber formulations for tires, conveyor belts, automotive parts, and cable insulation. It has been reported by the U.S. Environmental Protection Agency (1978) that tire manufacturers have increased the amount of antiozonants added to tires destined for the Los Angeles area.

Considerable research has been conducted to develop dose-response relationships between exposures of rubber to ozone, but it is not particularly pertinent to this discussion because most of the work has been done at elevated ozone levels with susceptible rubber formulations (without antiozonants). One exception is the work of Edwards and Storey (1959), who determined the effects of ozone at approximately 490 $\mu g/m^3$ on two styrene-butadiene rubber formulation at several levels of antiozonant. In the course of this work a damage function was developed relating the dose to produce visible cracks with the level of antiozonant in the rubber. In the chamber studies of Haynie et al. (1976) referred to earlier, rubber samples of the type used in the white sidewalls of top quality steel-belted tires were exposed to ozone at 160 and 1000 $\mu g/m^3$ and two levels of strain (10 and 20%) for 1000 hours. Table 1-11 from this work shows clearly that ozone concentrations, and to some degree strain, influence cracking rate.

1.5.2 Fabrics

In Section 1.4 it will be shown that nitrogen oxides can cause fading of fabrics and weakening of textile fibers. Ozone can produce similar effects. However, the same points about indoor exposure brought up in the section on nitrogen oxides are also applicable here. In addition, there are few sources of ozone indoors, and since ozone reacts rapidly with indoor surfaces, indoor concentrations are usually a very small fraction of those outdoors.

TABLE 1-11. CRACKING RATES OF WHITE SIDE WALL TIRE SPECIMENS

Ozone Concentration $\mu g/m^3$ (ppm)	Strain %	Mean Cracking Rate ± S.D.[a] $\mu m/yr$
160 (0.08)	10	10.36% ± 7.76
	20	11.70% ± 7.22
1000 (0.5)	10	19.80% ± 9.64
	20	24.09% ± 6.24

[a] S.D. = Estimated standard deviation of the mean.

Source: Adapted from Haynie et al. 1976.

While the effects of nitrogen oxides on fabric dyes were first noted before World War I, it was not until 1955 that Salvin and Walker (1955) showed similar effects from atmospheric ozone on specially developed blue disperse dyes designed to resist the effects of NO_2. However, ozone fading of dyes was manifested in a bleached or washed-out appearance rather than the reddening which is characteristic of the effects of NO_2 on the most sensitive dyes. These workers coined the term "O-fading" to describe this newly discovered phenomenon.

Salvin (1969) noted another type of fading on polyester-cotton/permanent press fabrics stored in warehouses in California, Texas and Tennessee in the United States. The combination of fibers and dyes were thought to be resistant to the effects of air pollution. After careful investigation it was found that the fading had occurred in dye which had migrated into the permanent press materials and not in the fiber itself. Salvin in this same work also showed that humidity is an important factor in ozone fading of textile fibers.

Beloin (1972 and 1973) carried out both field and laboratory exposures of several fabric-dye combinations. As was pointed out earlier, the field studies at several U.S. urban areas were not able to distinguish the relative effect of NO_2, O_3 or SO_2, but the controlled environment laboratory studies at 100 and 1000 $\mu g/m^3$ ozone showed fading. The higher concentration produced the greater fading. This study also confirmed that humidity and to a lesser extent temperature are factors in ozone fading of dyes. The chamber studies of Haynie et al. (1976) which included exposure of drapery materials also confirmed these results.

Cellulose fibers are susceptible to oxidation. Therefore one would expect that cotton and other cellulose-based fibers would be vulnerable to ozone attack. Bogarty et al. (1952) exposed samples of cotton duck and print cloth to air containing ozone in the range between 40 and 120 $\mu g/m^3$ in the absence of light. Samples were exposed both wet and dry. Damage was measured in terms of fluidity (reciprocal of viscosity) of dissolved samples of the cloth. An increase in fluidity indicates depolymerization from chemical attack (e.g., O_3, SO_2 or NO_2). Biological attack, while affecting fiber strength, does not change the average size of the fiber molecules.

After 50 days exposure, the cloth samples exposed to both ozone and high moisture levels showed increased fluidity. In addition, these samples exhibited a 20 percent reduction in breaking strength. The samples exposed dry to ozone showed no significant change. These workers believed that ozone's relatively high solubility in water promotes the action of ozone on cotton. But in spite of these results, they believed that ambient concentrations of ozone are a minor influence when compared with the effects of sunlight, heat, alternate wetting and drying, and biological attack. The work of Morris (1966) conducted at concentrations ten times higher than those of Bogarty but at ambient humidity levels showed no appreciable change in fluidity or breaking strengths.

Kerr et al. (1969) studied the joint effect of ozone and simulated washing-drying cycles on dyed print cloth over a 60-day exposure period. Ozone concentrations averaged 1500 $\mu g/m^3$. Breaking strength decreased 18 percent for samples exposed to both ozone and the wash/dry cycles compared to 9 percent for samples exposed only to the wash/dry cycles.

The work of Zeronian et al. (1971) showed that ozone at 400 $\mu g/m^3$ over a 7-day exposure period had no effect on modacrylic (Dynel) and polyester (Dacron) fibers and a slight effect on acrylic (Orlon) and Nylon 66.

1.5.3 Paints

The primary deleterious effect of ozone on paint is accelerated erosion of the paint film. Weight loss converted to thickness loss over a specified exposure period is the usual method of measuring this effect on test panels, thereby permitting a prediction of the life of the film through extrapolation of the exposure data.

There are two research efforts that represent the bulk of knowledge on the effects of ozone on paints. These studies were mentioned in Section 1.2.3. Campbell et al. (1974) at the Sherwin-Williams Paint Company carried out both laboratory and field studies on five different types of paints: oil and latex house paints, urea-alkyd coil coating, nitro cellulose/acrylic automotive paint, and alkyd industrial maintenance coating. Spence et al. (1975) at the U.S. Environmental Protection Agency conducted laboratory chamber studies on four classes of painted surfaces: oil base house paint, vinyl-acrylic latex house paint, vinyl coil coating, and acrylic coil coating.

In the laboratory work of Campbell et al. (1974) exposures both shaded and unshaded at 2000 $\mu g/m^3$ produced measurable erosion effects with oil-based house paint showing the greatest erosion rate; the industrial maintenance coating showed a moderate erosion rate; and the latex, coil and automotive coatings showed the least effect. The unshaded samples, as one would expect, showed the greatest erosion rates. Exposures at 200 $\mu g/m^3$ did not produce statistically significant erosion rates. In this same work, field exposures at several United States locations did not produce as clear-cut results as the laboratory tests; however, the higher erosion rates of paints exposed in Los Angeles as compared with other locations were ascribed to higher ozone levels as compared with other locations.

The Spence et al. (1975) study was designed to show the separate and joint influence of several gaseous pollutants (SO_2, O_3 and NO_2) and other environmental factors. Statistically significant effects of ozone were measured for the vinyl and acrylic coil coating. The oil-based house paint contained a calcium carbonate filler which was strongly affected by moisture and SO_2. This effect masked any possible effect by ozone on this paint.

A damage function for acrylic coil coating at 90 percent relative humidity was developed as follows:

Erosion rate = $0.159 + 0.000714\ O_3$ where erosion rate is in $\mu m/yr$ and O_3 is in $\mu g/m^3$.

While the effect of ozone on this type of coating is statistically significant, it is somewhat academic because at an average O_3 level of 100 $\mu g/m^3$ this function predicts that a 20 μm-thick film would last over 80 years.

1.6 OTHER POLLUTANT EFFECTS

The foregoing sections have described the effects of those criteria pollutants which are capable of producing effects on materials. Volatile organic materials and carbon monoxide are believed to have no significant effects on materials. However, several other gaseous pollutants that have from time to time been emitted from industrial and natural sources should be briefly noted.

1.6.1 Hydrogen Sulfide

Hydrogen sulfide can be emitted from a number of anthropogenic sources: polluted salt water, coke making, oil refineries, pulp and paper manufacture, chemical manufacture and other sources. Natural sources include decomposing vegetable and animal matter, volcanoes and geothermal operations.

Yocom and Upham (1977) have summarized some of the effects on materials which include tarnishing of non-ferrous metals, discoloration of lead-based paint, and damage to electrical contacts. While such problems have been noted in the past in many urban areas, control of H_2S sources and changes in exposed materials (e.g., use of titanium oxide rather than lead oxide in paints) have significantly reduced their severity in recent years.

1.6.2 Fluorides

Hydrogen fluorides and other fluorine-containing materials are emitted from a number of industrial processes including glass or frit manufacture, fertilizer production, and aluminum manufacture. Under extremely high concentration levels, HF and SiF_4 can etch glass and other high silica materials. Some experiments have been conducted that demonstrate this effect (Robinson et al., 1972). One would also expect other types of material damage, especially metal corrosion, at these high levels. However, efforts to control fluoride emissions because of the extreme sensitivity of vegetation to fluorides have essentially eliminated any problem of material damage from ambient concentrations.

1.6.3 Ammonia

Ammonia occurs in the atmosphere from natural sources, especially anaerobic decomposition of proteinaceous material and from a number of industrial processes, e.g., by-product coke manufacture and a variety of chemical processes.

However, its extreme solubility in water and ability to react with acidic components of the atmosphere assure that it normally exists in low atmospheric concentrations except near strong sources (National Academy of Sciences, 1979).

At high concentrations ammonia can corrode a number of non-ferrous metals such as copper, tin, zinc and their alloys. Ferrous alloys are generally resistant, but stress corrosion can be produced in carbon steels.

Ammonia, again at high concentrations, can soften wood through interaction with cellulose fibers and can soften natural rubber. Some plastics also can be adversely affected by ammonia, notably epoxy fiberglass, nylons and polyvinyl chloride under certain conditions of temperature and concentration.

In general, ammonia is not a significant air pollutant with respect to material damage.

1.7 REFERENCES

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2. ECONOMIC ESTIMATES

2.1 INTRODUCTION

Society is faced with the difficult task of balancing the benefits it may gain by reductions in pollution levels against the economic and social costs of obtaining those reductions. To facilitate finding the proper balance, the relationships between pollution and its effects are often stated in common terms. The quantitative expressions of such relationships in monetary terms are called economic damage functions.

Economic theory states that a control policy is optimal if the marginal benefits due to pollution abatement is matched by the marginal expenditure incurred to implement the control (Liu and Yu, 1979). The benefit due to pollution abatement is commonly stated as the inverse of the dis-benefit or cost of the damage due to the pollutant in question.

While the assignment of monetary value to such pollution-related effects as illness, ecological diversity or even life itself is a controversial approach, monetizing damage to non-living materials is seen as inherently more acceptable and appropriate. Even though materials damage is only a part of the total dis-benefit of pollution, its quantification is an important part of the overall analysis of costs.

Unfortunately, the current ability of society to accurately relate the costs of damage to materials to the level of ambient pollution is poor. There are great uncertainties about the physical mechanisms and degree of the damage attributable to pollutants, even greater uncertainties about the economic impact of that damage and much fundamental information such as the level of ambient pollution itself, is often inadequate. The existing state-of-the-art for employing economic damage functions in rational decision making is such that only crude, qualitative use of such results is appropriate.

Economic estimates of the costs attributable to some of the damaging effects of sulfur oxides and particulate matter on materials are available from the literature. Some of these estimates were derived directly from consumer or business surveys. Others were derived from estimates of maintenance and replacement costs based upon available damage functions and ambient air data. Extrapolation of these study results for application to the present situation is not easily done, and in some cases cannot be done with accuracy, since both fluctuations in the value of the dollar in the intervening years and changes in air quality must be considered in any such adjustment of past reported dollar cost of materials damage. Therefore, in the present document, all dollar costs assigned to materials damage and soiling are given as reported.

Table 2-1 presents a summary of the Consumer Price Index for the years from 1966 to 1980. In the table, 1967 is used as the base year and is set at 100. All other years reflect prices relative to 1967.

TABLE 2-1. INFLATION ADJUSTMENT

1980	251.7
1979	217.4
1978	195.4
1977	181.5
1976	170.5
1975	151.2
1974	147.7
1973	133.1
1972	125.3
1971	121.3
1970	116.3
1969	109.8
1968	104.2
1967	100.0 (Base year)
1966	97.2
1965	94.5
1964	92.9
1963	91.7

2.2 TYPES OF ECONOMIC DAMAGE

The costs of air pollution damage to non-living materials fall into three general categories: direct damage costs, avoidance costs and aesthetic or psychic costs (Stankunas, 1980); each of these categories can be quantified in monetary terms. However, the complexity of determining those costs increases with the extent that human judgment plays a role in the actions taken.

When physical damage has proceeded to the point where the material in question no longer serves its intended function, the cost of that damage can be directly derived from the cost of replacement or repair of the material. For example, when a metal storage tank becomes so corroded due to pollutant damage that it begins to leak, the cost of fixing the leak or of replacing the tank is obvious. The human judgment factor is primarily concerned with the desirability of having the storage tank at all. The direct damage has a direct response, and the direct response engenders a direct cost.

In real-world practice, however, allowing materials to degrade until they no longer fulfill this primary function is seldom the norm. The value of a structure or a system is usually greater than the simple sum of its component materials. Accordingly, it is common practice to expend effort and money to avoid deterioration if the continual use of the overall structure is important. Protection of damage-susceptible material or substitution with similar but more resistant materials is the usual alternative. When the protection or substitution results in higher costs, those costs can be attributed as an avoidance cost of the damage.

Avoidance costs are harder to quantify accurately than direct damage costs. Human judgment is needed to determine the best strategy for avoiding damage. The problem is especially acute when substitution of different materials is considered. The new material often has different properties beyond increased resistance to damage by pollutants. For example, if a stainless steel tank is substituted for an ordinary carbon steel tank, a whole collection of physical properties changes. The method of fabrication, the basic design, size, or shape may be different in turn. The non-reactive nature of stainless steel may make it a superior container for the substances stored within it. If the stainless steel tank is more desirable than a carbon steel one for a number of reasons, the fraction of the cost which should be assessed to its increased resistance to atmospheric pollution may be hard to quantify.

Similarily, protection of a susceptible material can change more than the reaction to pollutants. Painting a surface can also change its color or appearance. Determining the fraction of the full cost of the paint job attributable to the increased resistance to pollution it affords the substrate is not a simple task.

It should also be noted that the paint can be considered a material susceptible to pollutant damage in its own right. It, in turn, can be the subject of direct damage costs in the case where replacement (re-painting) is necessitated by pollutant damage, or of avoidance costs when a more expensive formulation is substituted for one with less pollution resistance.

Aesthetic costs are by definition based on human judgment. They are also the most difficult to quantify and are the most variable with location and/or time. Despite their somewhat subjective basis, such costs are important in assessing the dis-benefits of pollution.

Aesthetic costs are, at least in part, reflected by the costs paid to avoid them. People are willing to pay to maintain or restore a material to a state which has little to do with its ability to perform its primary function.

A metal storage tank holds as much whether its outer surface is clean or dirty. Yet, the increased cost of keeping it "reasonably" clean reflects the fact that there is some psychic cost in seeing it dirty.

Quantifying this psychic cost is extremely complicated. The price paid to avoid the psychic cost is real, but it is also a function of changing notions as to what is "acceptable". The willingness to pay is often tempered by the ability to pay. Finally, the "acceptability" of a situation is often based on some dimly defined sense of economic utility. Rust stains may be unsightly because they indicate an underlying physical damage which could lead to loss of function of the material in question.

Aesthetic costs exist even if no monetary expenditure is made to eliminate them. However, they are nearly impossible to quantify accurately.

In summary, each category of cost contains some element of human judgment which influences the responses made to it. The more the human element is involved, the more difficult it is to quantify the cost in monetary terms. Economic damage functions which fail to account for the different types of costs do not provide useful information for decision-making.

2.3 METHODS FOR CALCULATING ECONOMIC IMPACT ON MATERIALS DAMAGE

2.3.1 Comparative Approach

There are two basic approaches for calculating the economic disbenefit due to a given air pollutant; these may be termed Comparative and Analytic (Stankunas et al., 1980). Neither method is completely satisfactory. The Comparative approach compares the lifetime or maintenance costs for a given material in use in different ambient pollution environments. For the method to work, the environments should be similar in every respect, except for pollutant level. The total materials costs in each of the environments is determined and an economic damage function for the pollutant can be derived directly using the differences in materials costs and the differences in pollutant concentration.

There are several factors which make the comparative approach difficult to apply. The approach is highly sensitive to differences in the nonpollutant variables at each location. Since there are so many variables which can have a strong influence on materials damage and materials costs, it is extremely difficult to find locations that are truly well matched. Environmental and usage factors for the same material can be so different that the whole mechanism of damage may be changed. These problems lead to the necessity for examining a large number of matched environments in order to cancel out "random" errors. "Approximations" and "simplifying assumptions" can obliterate the true cost information being sought.

2.3.2 Analytic Approach

The Analytic approach depends on laboratory or field-study derived physical damage functions and ambient air quality information. First, the specific interactions of the materials to be studied with the pollutants of interest must be delineated. The use of these materials and their value in society must be assessed. The exposure of the materials to pollutants and other environmental factors must be determined, as well as the effects of repair, replacement, protection, substitution practice, and the aesthetic sensitivity of the population concerned. The appropriate physical damage functions are used to quantify the physical damage due to a specific pollutant. The costs of that damage, relative to the degree of pollution actually present can then be calculated.

The success of the analytic approach is dependent on the accuracy of each of its component parts. Its chief drawback is the unavailability of needed data inputs. Much of the necessary information must be approximated or estimated from widely disparate sources. For example, the amount and value of materials in place in an area or on a nationwide basis is not readily available information, and the amount of material "in place" is a key input to economic damage functions.

In past studies, the amount of material exposed has been calculated by determining the amount produced during a period equal to the standard "use-life" of that material, and application of an "exposure factor" to account for the uses of which the material is put (Waddell, 1974). (The derivation of "exposure factors" is often surprisingly arbitrary.)

Such a methodology has several major flaws. The most serious flaw is the inherent assumption that once a material is in place, it remains unchanged, except for deterioration. In some cases, such an assumption may be warranted, but in others it totally ignores the impact of practices related to avoidance costs and the changes in those practices with time. Galvanized steel is a good example. Not only has pollutant damage to galvanized steel been well studied (Haynie, 1980), such damage constitutes a major fraction of the costs attributed to pollution in many Materials Damage estimates.

Zinc coating is added to protect the steel from corrosion (note that the zinc coating would still be needed to protect steel against natural corrosion even if there were no man-made pollutants to consider). For many years galvanized surfaces were not otherwise coated due to poor paint adhesion. During the last 10 years, however, numerous paints and coatings have been introduced into the market which not only adhere to galvanized steels, but also offer excellent pollutant resistance. When bare galvanized steels may be susceptible to pollutant attack, coating such materials (especially for roofing and siding applications) is now common. When a galvanized steel surface shows signs of rust, it is now possible to avoid further damage instead of simply waiting until it is severe enough to warrant replacement. Therefore, although galvanized products are still in extensive use, the amount of zinc actually exposed to pollutants has greatly decreased, a factor not considered in most materials damage estimates to date.

The value of the material in place, or the costs associated with keeping it there, are likewise uncertain. Calculating the value of labor input to the cost of direct damage to a material is much more complicated than determining the cost of the material alone. Most studies to date have simply applied a "labor factor" to the overall estimate of the material replaced (Salmon, 1970). Since labor costs often dominate materials costs, any uncertainties or errors in estimating a "labor factor" have a major impact on the accuracy or certainty of the final cost estimate.

The reasons and schedules for maintenance activities can have a powerful effect on how the costs should be apportioned. For example, highway bridge steel is painted primarily to protect against corrosion. A physical damage function for attack by SO_2 on the paint can be derived. However, the paint is also subject to damage from rock impact, salt, and exhaust, etc. To resist damage from these much more severe damage agents, the paint is made especially tough and thick. Before air pollution can even begin to significantly affect the performance of the paint, it will usually have been damaged by the rocks, salt, or other environmental factors, such that maintenance action is necessary. The maintenance required by this other damage will also repair any minor damage that SO_2 might have caused. Therefore, the effect of SO_2 on the lifetime of the paint is minimal, except indirectly as a result of corrosion of steel by SO_2. Corrosion of the underlying metal may cause undercutting and peeling, which would lead to more frequent painting. The physical damage is below the threshold where it would have an effect on the bridge maintenance schedules or costs.

Similarly, children's shoes are rarely discarded because of SO_2 damage, although the leather may have a measurable damage function. It is possible to think of hundreds of other examples where a pollutant could cause damage, but other factors control the material's useful life. In assessing damage costs, proof of the existence of a damage mechanism by a given pollutant is not sufficient to say the damage is significant. If must also be shown that the pollutant has a real influence on the use life of the material (Stankunas et al., 1980). Unless the analytic approach specifically takes into account the principal lifetime controlling factors, the damage cost estimates it generates are almost useless.

The usual practice when reporting costs based on the analytic approach is to give a range of error expected. Based on the accumulated uncertainties, the range of error often encompasses factors of ten or more (Stankunas et al., 1980). Sadly, the statements of uncertainties are often overlooked when people begin to use the calculated values for decision making.

2.3.3 Alternative Approaches Under Development

Freeman (1979b) noted that in the materials damage area, "the weakest link in most of these (materials damage cost) studies is the estimation of quantities of material at risk and exposure levels." While further application of the exposure inventory (Stankunas et al., 1981) approach may provide information necessary for more reliable application of the physical damage function approach, new approaches to estimating the cost of pollutant effects on welfare, including materials damage, have been recently developed.

Manuel et al. (1981) developed an estimate of benefits to be realized from reductions in ambient SO_2 and TSP concentrations. They drew heavily on econometric analysis to identify the influence of changes in TSP and SO_2 levels on certain production and consumption decisions of selected components of the agricultural, manufacturing, household, and electric utility sectors of the economy. The approach allows consideration of substitution possibilities by both buyers and suppliers. Indexes of decision behavior of decision-making units within each sector were chosen to reflect the effects of TSP and SO_2 on agricultural yield, materials damage, and soiling.

The theoretical approach and empirical methods employed appear to be well based. However, additional analysis of the study's results are needed to explain more fully certain implied behavioral adjustments. In addition, more extensive air quality data and more detailed economic data would have permitted not only greater coverage but may also have served to reduce the degree of uncertainty associated with the estimated benefits.

2.4 SPECIFIC ECONOMIC DAMAGE FUNCTIONS

2.4.1 Choice of Materials

So many materials are currently in use where they are exposed to pollution, it is not practical to attempt to quantify all damage costs due to all pollutants. There are two basic approaches to limiting the number of combinations to be considered. A number of materials could be chosen for study on the basis of their economic importance and the list limited by considering only those which evidence significant reaction with common air pollutants. Conversely, a list of materials which are known to respond to air pollution exposure could be drawn up, and the list subsequently limited only to those which are economically important. The key is that the final list should contain those materials for which pollution exposure has a serious impact on economic utlization. To warrant detailed study, a material should be both affected by the pollutant of interest and of economic importance. It makes little sense to detail the costs of damage that SO_2 does to buggy whips, even though the leather in them is susceptible to SO_2 damage. At the same time, too much effort should not be expended examining highway paving for oxidant damage just because highways represent major cost items.

Annual production figures have limited usefulness in determining the economic impact of a given material. Such figures do not take into account the use for which the material is intended, and do not include the costs associated with its utilization (installation labor, maintenance, etc.). Furthermore, use of such figures can lead to significant "double counting," (i.e., materials sold to producers of other materials).

Perhaps most importantly, if only materials with very high annual production are considered, materials with somewhat lower total production, but higher loss rate due to pollutant damage may be missed. This phenomenon is particularly important if most of the turnover of the lower production material is due to pollutant damage.

Existing information about physical damage functions and previous studies claiming significant economic impacts of pollutant damage leads to the list of materials in Table 2-2. In some cases, the designation of significant economic impact may be inaccurate or at best highly uncertain, but these materials are included in the discussion because the values reported have received such widespread note.

TABLE 2-2. ECONOMICALLY SIGNIFICANT MATERIALS SUBJECT TO POLLUTION DAMAGE

Paint
Structural metals
Electrical components
Fabrics
Plastics and elastomers
Non-metallic building materials
Works of art and historical monuments.

2.4.2 Paint

Types of damage: Surface erosion, discoloration, soiling.

Principal damage-causing pollutants: sulfur oxides and other "acid" gases, particulate matter

Other environmental factors: moisture, sunlight, physical abrasion (wear), microorganisms.

Uses: The principal function of paint is to protect a subtrate and, as such, the cost of the paint and the labor and other costs associated with applying it can be considered an "avoidance cost" of damage to the substrate. However, a significant secondary function of paint is to enhance the external appearance of the structure or material to which it is applied. In this regard, paint is a "material" in its own right, and steps are taken to maintain its condition beyond that necessary for it to fulfill its protective function.

Because of this dual nature, care must be taken not to double count damage costs when paint is subject to attack by pollution. That is, the costs of damage to paint when paint is considered as a protective measure for a sensitive substrate such as carbon steel should not be totally counted as a cost of pollution if the cost of the same damage is to be counted as a loss of appearance of the paint itself.

Cost categories:

Direct: The most common type of action taken when one of the functions of a paint surface is impaired is to repaint or replace the paint. This approach is especially prevalent if the characteristic impaired is its protective function. Repair of a paint surface by "touch-up" painting or by cleaning of a soiled surface is sometimes practiced but is not as common since the labor costs can be close to those for repainting and the cost of the material itself is relatively small in comparison.

Avoidance: Paint as a material is not "protected" by the application of other materials or by changing its exposure to pollutants. The primary cost avoidance strategy is substitution. The formulation of the paint is changed and so a "new" paint is substituted. Note that substituting a completely different type of material (e.g., aluminum siding) in place of paint as a way to protect the substrate structure is not a case of "substitution" for paint *per se*. If a different type of material is used, the properties of the system are such that the discussion no longer involves paint at all. Just as the automobile cannot truly be considered a "substitute" for the horse or the horse a "substitute" for human legs, a major change in the nature or category of a material is more than a substitution. The portion of costs related to air pollution damage associated with a major substitution should be considered as an alternate protection strategy for the substrate being protected. These changes generally show up in the consideration of the amount of material in place.

Aesthetic: As with most disamenities, damage to paint is difficult to quantify monetarily. Some idea of the value of the aesthetic properties of a well maintained painted surface can be obtained by analyzing the direct and avoidance costs for damage to the non-protective aspects of paint. That is, the fact that society in general is willing to pay to maintain painted surfaces in a clean condition indicates there is a psychic penalty paid by those who see it dirty. However, since the acceptability of a given condition varies widely among individuals and with time, and with many other subtle influences, it cannot generally be quantified with any confidence.

Previous studies: Spence and Haynie (1972) presented a survey and economic assessment of the deterioration of exterior paints ("trade paints") caused by air pollution. Included in this category were both oil-base paints and latex paints containing polyvinyl acetate-acrylic as the binder. The total annual economic damage to exterior household paints was estimated at $540 million (1972 prices), including paint loss and a labor factor of three times the cost of the paint.

Salmon (1970) estimated that the annual cost of soiling of household paint would be $35 billion if surfaces were maintained as clean as they are in a clean environment (aesthetic costs). The annual cost of deterioration damage to paints was estimated to be $1.2 billion (direct costs). A 1974 study by Midwest Research Institute (Waddell, 1974) recalculated the annual cost of damage to be $22 billion for soiling and $753 million for deterioration. These figures appear to be based on Salmon's hypothetical situation evaluation, which has been criticized as unrealistic. With a total cost of $2.5 billion for annual production of household paints, the damage far exceeds the production cost, even with a labor factor of 6 to 8.

Michelson and Tourin (1967) investigated the frequency of house repainting as a function of suspended particulate concentration using a Comparative approach. Questionnaires were sent to residents of three suburbs of Washington, DC (Suitland, Rockville, and Fairfax) and two cities in the upper Ohio Valley (Steubenville and Uniontown). Data were compiled from the questionnaires to show maintenance intervals for exterior repainting in each of the five communities, but paint types were not reported. In Steubenville, where the mean annual particulate concentration was 235 $\mu g/m^3$, the estimated repainting frequency was greater than once per year. In Fairfax, where the mean annual particulate concentration was 60 $\mu g/m^3$, repainting occurred every 4 years. Thus, maintenance frequency increased as particulate concentration increased, as shown in Figure 2-1 (Michelson and Tourin, 1967). Such a linear function seems suspicious since a plateau at the low and high extremes of particulate concentration should be expected. The results of this investigation suggest

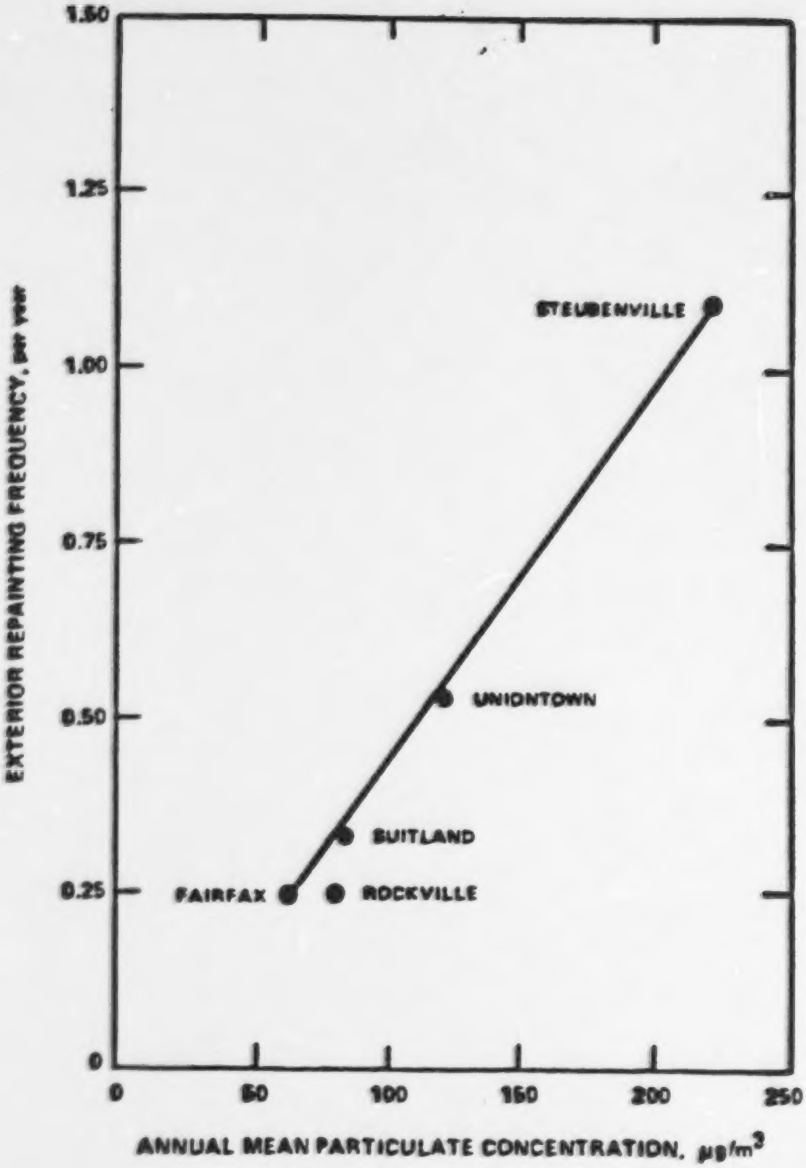

FIGURE 2-1. Indicated relationship between maintenance frequency for exterior repainting and particulate concentration.

Source: Michelson and Tourin (1967).

that although a significant relationship exists between frequency of repainting and particulate concentration it is difficult to quantify by simple survey techniques. The survey results may have been skewed by the fact that people who had repainted recently were more likely to respond than those who had not.

It would appear that additional maintenance data are needed, particularly for cities with mean annual particulate concentrations greater than 150 $\mu g/m^3$, to establish a more definite correlation. In addition, any correlation of frequency of repainting with concentration of particulate matter must take into account the fact that SO_2 is usually present in high concentration where particle counts are high. Thus, the cities in question were not sufficiently well matched for a simple comparative analysis.

Booz Allen and Hamilton (1970), in a study conducted for EPA, reported on painting maintenance frequencies in several zones of the Philadelphia metropolitan area with different population characteristics, climates, and types of industry. Socioeconomic factors were delineated by pollution zone; however, paint types were not reported. The percentage of households with incomes of less than $6000 increased with pollution level, a finding that may partially explain why there was no statistically significant correlation between painting frequency and particulate level found.

Stankunas et al. (1981) developed a geographically distributed inventory of exposed materials in the Boston metropolitan area. Isopleths for SO_2 were laid over a map reflecting exposed materials. Damage functions were applied to determine an estimate of SO_2 effects on materials for the entire area. Cost factors for repair were applied; the resulting annual cost estimate for SO_2 damage to paint in the Boston area was $31 million. For bare galvanized metal, the annual cost due to SO_2 was reported to be only $335,000. The authors noted that the amount of exposed bare galvanized metal and of structural concrete was low when compared to exposed painted surfaces. They also pointed out that the paint damage costs were derived using a damage function for oil-based house paint. Its applicability is questionable due to the widespread shift to SO_2-resistant latex paints.

2.4.3 Structural Metals

Type of damage: Corrosion, tarnishing.

Principal damage agents: SO_2, NO_x, TSP, other acid gases.

Other environmental factors: Moisture, salt.

Use of the material: The material is widely used in a variety of applications from tanks, buildings, and structural supports to roofing and vehicles. The material is generally selected due to its high strength per unit area and its durability rather than any aesthetic considerations.

The structural materials susceptible to damage by air pollution are zinc (galvanized), steel, and iron. Nonferrous metals such as aluminum and copper, are relatively resistant to corrosion in the presence of air pollution, however, some studies have found that stress corrosion may be a more serious problem under some applications (The Research Corporation of New England, 1976).

Cost categories:

Direct: Both replacement and repair strategies are used in response to damage to structural metals. The relative importance of each in a given situation depends on factors such as the effectiveness of repair in restoring complete functionality, the ratio of material costs and labor costs and especially on the economic lifetime of the structure made of the material in question. Structures or objects with economic lifetimes shorter or on the same order as the physical lifetime without repair are often allowed to deteriorate until replacement is required. However, in such cases, the effect of air pollution damage on the total lifetime is generally small. For example, automobiles usually suffer damage leading to a reduction of economic life from general wear and corrosion due to salt, moisture and abrasion much greater than that due to air pollution.

Avoidance: Costs for protection often constitute the major cost category for pollution damage to structural metals. The most common protection strategy is zinc coating (galvanizing) and/or painting. Costs for painting are especially important since a higher portion of such costs can be directly attributed to avoidance of pollution induced damage.

It should be noted that painting does not completely eliminate damage to metals. Defects in the paint surface, such as pin-holes or thin spots, can leave small areas effectively unprotected. Subsequent attack of the substrate leads not only to direct physical damage to the substrate, but accelerated damage to the rest of the protective coating. Thus, extra costs for surface preparation as part of an overall damage avoidance strategy are usually justified (Stankunas, 1980).

Aesthetic: As with painted surfaces, the aesthetic cost of seeing an "unsightly" corroded surface is real but difficult to quantify. In fact, new steel alloys which form a non-damaging coat of oxidation products are rapidly being seen as aesthetically pleasing. An ironic twist is that such steel alloys actually require a small amount of sulfur oxide pollution in the air in order for the surface to form properly. If such material is used in a pristine environment, it suffers unacceptably rapid deterioration.

Previous studies: Spence and Haynie (1974), in a chamber study of the effects of pollutants on galvanized steel, determined that clean air corrosion rates ranged from 1.14 μm/yr to 37.17 μm/yr over a range of relative humidities and temperatures.

The corrosion rates for clean air and polluted air were found to be very similar, however, the corrosion function which occurred was different for the clean atmospheres. In the case of the clean atmospheres the corrosion function was described as "pitting" as a result of the moisture nucleation at the end of wet and dry cycles. Galvanized steel in the outdoors, when only partially dry will develop this type of pitting regardless of the absence or presence of SO_2. The authors concluded that the corrosive effects of polluted environments on galvanized steel are not additive to the corrosive effects noted under clean air conditions. However, corrosion due to both "clean air" interactions noted in the experiments and that due to SO_2 will occur simultaneously during outdoor exposure of steel panels in the real world, making it difficult to distinguish material damage due exclusively to SO_2 concentrations.

Possible synergistic effects on metals have been found in atmosphere containing particulate and SO_2, as well as ozone and NO_x. Thus it is very difficult to isolate separate effects due to natural occurrences and air pollutants on materials exposed outside.

Damage estimates and subsequent economic costs due to the effects of air pollutants on material suffer from a large number of flaws. A typical cost estimation approach, such as the one performed by Salmon (1970), uses annual production of the material multiplied by a hypothetical factor (representing the assumption of exposure). No allowance is made for those materials upon which protective coating, such as paint, is applied or for naturally occurring degradation.

Painting of structural steel in bridges was investigated by Moore and O'Leary (1975); the practice involves sandblasting the steel to produce a rust-free surface and to remove mill scale. Without such surface preparation, water is immediately absorbed and sets up a corrosion system, rusting occurs, and the paint surface deteriorates in 2 to 3 years. The metal surface is protected by a primer that inhibits rust formation, and the primer coat is covered with two coats of SO_2-resistant paint, such as vinyl resin, which is substantially more expensive than household paint. Banov (1973) estimated the cost of sandblasting at 25¢/ft^2 and the total labor cost at four to five times the cost of the paint. The cost of painting structural steel to give a service time of 10 years or more in urban areas can be as high as \$1 to \$1.25/ft^2. Michelson and Tourin (1967) estimated the extra cost of paint application on external steel structures at \$250 million.

A recent study published by the U.S. Department of Commerce (Bennett et al., 1978) estimated that metallic corrosion cost \$70 billion in the United States in 1975. This study used a modified version of the Battelle Columbus Laboratories National Input/Output Model, and the results were subjected to an uncertainty analysis by the National Bureau of Standards. The model, which incorporated a broad range of cost items (e.g., materials, labor, energy, and technical capabilities), indicated a total annual corrosion cost of \$82 billion. However, the cost of corrosion specifically associated with ambient air pollution was not separated from other types of corrosion. Uncertainty in the total corrosion cost figure was estimated at ± 30 percent. Analysis suggested that avoidable costs of metallic corrosion represent about 15 percent of the total, but could range from 10 to 45 percent.

The National Commission on Materials Policy (Yocom and Grappone, 1976) estimated that \$5 billion could be saved annually by using known procedures to decrease corrosion of industrial steel, such as sandblasting the surface before painting and applying two coats of paint, which would protect the metal for many years with little maintenance. Fink et al. (1971) estimated that corrosion caused by air pollution of external metal structures costs \$1.45 billion annually.

2.4.4 Electrical Components

Type of damage: Corrosion, tarnishing.

Principal damage agents: SO_x, NO_x, other acid gases, polymerizable organic gases, particulate matter.

Other environmental factors: Moisture, salt.

Uses of the material: Contacts and components are made from a wide variety of metals; primarily gold, silver, and copper. Air pollutants can cause an insulating film to form on the metal components, resulting in failure of the components. Accumulation of particulates can cause defects in manufacturing or, in extreme cases, short circuits in components in use.

Cost categories:

Direct: Since the costs associated with the loss of service of electrical components is so high, damage extensive enough to necessitate replacement or repair is rarely allowed to accumulate. Problems with electrical components functioning in polluted atmospheres were recognized in the distant past, resulting in design changes and use of different materials which function adequately in these environments. For example, when the relay springs in telephone exchanges began to suffer breakage due to nitrate induced stress corrosion, a new spring alloy was developed and the problem ceased to be important. This one-time direct cost to solve the problem is not a significant cost of air pollution damage when such costs are averaged of a period of years. The costs of the new spring alloy were not significantly different than for the old one so there is not even a continuing avoidance cost. In any case, new solid state switching technology has largely supplanted mechanical relays and made the whole question moot.

Avoidance: Costs to avoid damage constitute the major category of pollutant damage costs. The greatest portion of these costs is attributable to protection (in the form of enclosed, controlled environments) and substitution of non-corroding materials (generally precious metals) for simple conductors. In both cases, the degree of damage acceptable is so low that similar if not exactly the same measures would be necessary even in the absence of significant ambient air pollution.

Aesthetic: Since most electrical components are primarily utilitarian, little to no aesthetic costs are incurred by their damage.

Previous studies: Robbins (1970) estimated that 15 percent of the gold and platinum used in the United States for electrical contacts in 1970 was for the specific purpose of combating SO_2 corrosion, with the remainder going for protection against other environmental pollutants. The use of palladium in electrical components has presented a problem in that it acts on compounds derived from plastics to catalyze the formation of an organic polymer film which acts as an insulator.

In areas where electrical instrumentation and computers are used, air is dehumidified and purified to help protect against corrosion. Robbins (1970) suggested that the use of activated carbon filters and high-efficiency fine particle filters represents a cost attributable to SO_2 and particulate contaminants, as itemized in Table 2-3.

TABLE 2-3. COSTS ATTRIBUTABLE TO SO_2 AND PARTICULATE CONTAMINANTS IN THE ELECTRONIC COMPONENTS INDUSTRY

	Millions of dollars 1970
Use of precious metals	20
Protective measures--filters and air conditioning	25
Loss due to failures	10
Research	5
Total	60

These estimates may overstate the costs since the benefits gained from the actions taken extend beyond protection from SO_2 and particulate matter. In addition, since the physical damage function is not a single linear relation of damage and concentration, (i.e., even the smallest amount of damage is significant), the costs are likely to be unchanged by any feasible reduction in pollutant level, and can thus be considered independent of pollution.

2.4.5 Fabrics

Type of damage: Reduced tensile strength, soiling, fading.

Principal damage agents: SO_2, NO_2, O_3, TSP, other acid gases.

Other environmental factors: Sunlight, moisture, temperature, mildew, physical wear.

Uses of the material: Fabrics are used both indoor and outdoor in clothing, home furnishing, etc. The costs associated with pollution effects on fabrics can be determined from the outdoor exposure of material, which is extremely limited. For clothing and other textile materials used indoors, air pollution can only be considered a real factor for curtains.

In most cases, the economic lifetime of fabrics and textiles is so low that economically significant pollution damage is minor.

Cost categories:

Direct: Replacement and repair of fabrics is usually so dominated by physical wear or style that most pollution induced degradation is negligible. Rare instances of extreme pollution episodes leading to short term damage such as runs in nylon hose or tearing of heavier fabrics are generally associated with special and localized problems and not general ambient air quality. Accidental releases of acid mists and smuts are typical of such cases.

The only significant chronic problem with fabrics attributable to ambient air quality is soiling. Such soiling is generally indirect, that is it results from contact with surfaces which had been soiled over relatively long time periods. Since the direct costs of cleaning soiled fabrics depends on a number of individual tastes and standards, they are extremely difficult to predict as a function of ambient pollution level.

Avoidance: There is little that can be done to avoid pollutant damage to fabrics. The degree of damage is not generally sufficient to justify extensive air cleaning measures by themselves. Coatings which provide better soil release are generally used to protect against spills rather than direct or indirect air pollution impact. Substitution with more resistant materials is generally not implemented (except possibly in the case of reformulation of nylon polymers used in hosiery with more resistant varieties). In fact, the trend away from relatively resistant materials such as linen, wool and cotton toward more susceptible materials such as nylon and polyester indicates that the cost and other advantages of the newer materials outweighs the increased susceptibility to air pollution.

Aesthetic: The principal aesthetic cost is related to uncorrected soiled appearance and limitations on the colors or textures appropriate to life in a polluted environment.

Previous studies: The chief problem with prior economic estimates is that a large proportion of fading and physical wear were attributed to pollution rather than other environmental factors. Surveys of use and impact have found that:

- For most textiles, the lifetime of the material is determined primarily by the amount of exposure to sunlight, humidity level, and fashion changes rather than air pollution.
- For most indoor and outdoor textile soiling, leading to a greater frequency of washing or cleaning, is governed by factors other than TSP levels. The only major exception is likely to be curtains, in which case the cleaning frequency is more likely to be determined by habit rather than appearance.

- o There is, basically, very little realistic, quantitative information relating pollutant levels to loss of strength of different fabrics exposed at outdoor locations.

According to Brysson et al. (1967) high pollutant levels (mean sulfation 5 mg SO_3/100 cm^2/day and/or SO_2 concentrations of 0.2 ppm or 520 $\mu g/m^3$) can reduce the effective life to one-sixth when compared to low pollution sites (0.5 mg SO_3/100 cm^2/day and/or 0.02 ppm or 60 $\mu g/m^3$ SO_2 concentrations).

2.4.6 Plastics and Elastomers

Type of damage: Cracking, weakening.

Principal damage agents: Ozone, oxidants.

Other environmental factors: Sunlight, temperature.

Uses of the material: Plastics are used for a wide variety of material application ranging from automobiles to calculators. In the past plastics were considered as substitute materials for substances such as wood, leather, horn or shell, ivory, rubber, and paper. However, as the range of properties available in synthetic polymers increased and surpassed those of any previously known "natural" material, plastics began to be used for a variety of purposes made possible only by their existence. The state-of-the-art of polymer science is advanced to the degree that new materials are specifically designed for new uses. The result has been an incredible variety of uses for these materials and a high rate of change in both the materials in use and uses themselves. Due, in part, to the volatility of the situation, any estimates of economic damages on plastics is purely guesswork, since neither the damage function nor the exposure distribution are defined. In general these products are designed and built to function for periods of time consistent with their economic lifetime in polluted environments. Therefore, the economic loss due to the effects of pollution on these materials is minimal since an appropriate design factor has already been incorporated.

Cost categories:

Direct: The major fraction of direct costs is related to replacement rather than repair of plastics and elastomers. However, as stated above, the material is usually designed such that its response to pollution is not consequential relative to the economic lifetime of the product of which it is a part. A possible exception may be rubber tires. Increased side-wall failure can result from high ozone levels, especially in hot climates. However, the influences of sunlight and temperature are so strong that it is difficult to separate them from the pollutant damage and thus assess the role of pollution in increased costs.

Avoidance: Most cost avoidance strategies for damage to plastics and elastomers are built-in; that is, the formulation of the material itself was designed with pollution resistance in mind. The cost of such formulation considerations is difficult to define since the rapid changes in the field due to other factors results in such rapid turnover in materials use that few products are substituted strictly for air pollution reasons.

The most significant problem with understanding the effects of air pollutants on plastics is:

- the lack of data, since no studies exist to define cause and effect relationships;
- the overwhelming impact of environmental factors such as temperature and sunlight on the durability of the material.

Aesthetic: While some would consider the use of plastics itself an aesthetic cost, such an attitude is apparently not widespread. The short lifetimes associated with most plastic and elastomer products also reduce the likely aesthetic impact of any damage.

Previous Studies: No significant studies of the economic impacts of pollution damage to plastics and elastomers are available. Available information is generally based on unsubstantiated assumptions, and therefore are not useful to economic estimates.

2.4.7 Non-metallic Building Materials

Type of damage: Soiling, discoloration, surface breakage or spalling, rot.

Principal damage agents: TSP, SO_2, acidic gases.

Other environmental factors: Moisture, freezing and thawing, microorganisms.

Use of material: Brick, glass, concrete, stone and wood are used for both structural and decorative uses; therefore, the appearance, as well as the structural integrity, of each is important. Although dissimilar in many respects, each of these materials tends to be exposed to similar environmental conditions for similar purposes, that is they form the exterior shell of buildings.

Cost categories.

Direct: With the possible exception of marble, none of the materials has well defined physical damage functions for irreversible damage related to ambient air pollution. All can suffer from soiling and discoloration, and the costs incurred for changing can be significant. However, except for glass, changing is done on an infrequent basis and is generally not part of a routine maintenance program. These cleaning costs, like similar costs for other materials, are highly variable and dependent on aesthetic considerations. Since the cleaning of a building usually represents a major undertaking, an interesting inversion in normal practice is often observed. As TSP pollution decreases, expenditures for cleaning increase. At high pollution levels, the appearance is degraded so quickly that the cost of cleaning is not justified. As pollution levels decline, the forgone maintenance is perceived as worthwhile and is implemented.

Avoidance: In extreme cases, where pollution is rapidly causing degradation of buildings, such as the marble structures in Greece and Venice, protection of the surface with silicone oils or other coatings is being considered. However, these measures are only being considered for special structures and are not part of general practice. As discussed in other sections, substitution of one material for another with a number of significantly different characteristics is generally not considered a substitution strategy for avoidance of damage costs.

Aesthetic: The fact that some materials, such as light colored or carbonate rich stone are no longer considered suitable for building can be considered a potential aesthetic loss. However, as people become accustomed to, and eventually begin to prefer the materials which are more suitable, the effective sense of loss diminishes.

The inconvenience of soiling, especially on windows where a high degree of cleanliness is desirable, can be considered an aesthetic cost. However, in most cases it can be assumed that the costs incurred for cleaning is roughly sufficient to keep the uncompensated aesthetic costs low.

Previous studies: Although studies of the potential damage to substances such as concrete have produced high economic damage estimates, they are generally flawed to such an extent that their basic conclusions are of doubtful validity. The main problem is the lack of documented physical damage functions relating exposure to pollutants to significant damage. Simply assuming a given percent of the total maintenance and replacement costs is attributable to pollution damage is not sufficient or reasonable in the absence of data.

2.4.8 Works of Art and Historical Monuments

Type of damage: Fading, corrosion, spalling, soiling.

Principal damage agents: SO_2, NO_x, TSP, other acid gases.

Other environmental factors: Moisture, sunlight, temperature, physical wear.

Use of material: The types of materials involved represent an extremely wide variety ranging from metals and building stone to fabrics and paint. The type of damage suffered by an object is a function of the material of which the object is made and the way in which the importance of the object is affected by damage.

Cost categories:

Direct: Since some types of damage are irreversible and the objects destroyed are irreplaceable, there is a great concern regarding the loss of this historic and artistic value. The costs for these objects cannot be quantified due to their irreplaceable nature.

Even repair can destroy some of the intrinsic value of an art object or object of historical importance. Cleaning can be an important factor, but since preservation is often of higher importance than appearance, even this strategy is sometimes forgone to avoid damage.

Avoidance: The major monetary effect of pollution damage to art or historical objects is avoidance costs. Providing controlled, protective environments is a common practice and in some cases, application of protective coatings is attempted. Some portion of these protective measures are also useful in protecting against other environmental factors and should not be assessed as a cost of pollutant damage alone.

Aesthetic: By far the greatest cost incurred by society is the aesthetic cost of the loss or irreparable degradation of these objects. But since such costs grow even greater with the passage of time, and there is no definable economic lifetime for a truly important work of art or historical object, the total costs are incalculable.

Previous studies: Although damage to works of art and historical objects has been addressed in general terms by Yocom and Grappone (1976), no thorough attempt has been made to quantify the economic loss suffered due to air pollution effects. Due to the complex and aesthetic nature of the problem, there is some doubt whether such an estimate is possible.

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